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⑪ Publication number:

0 395 199  
A1

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## EUROPEAN PATENT APPLICATION

㉑ Application number: 90301963.6

㉓ Int. Cl.<sup>5</sup>: C07C 23/34, C07C 69/608,  
C07D 303/04, C07C 57/26,  
C11B 9/00

㉒ Date of filing: 23.02.90

㉔ Priority: 28.04.89 US 345014

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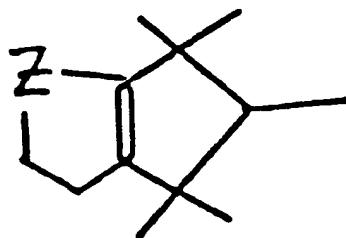
㉕ Date of publication of application:  
31.10.90 Bulletin 90/44

㉖ Designated Contracting States:  
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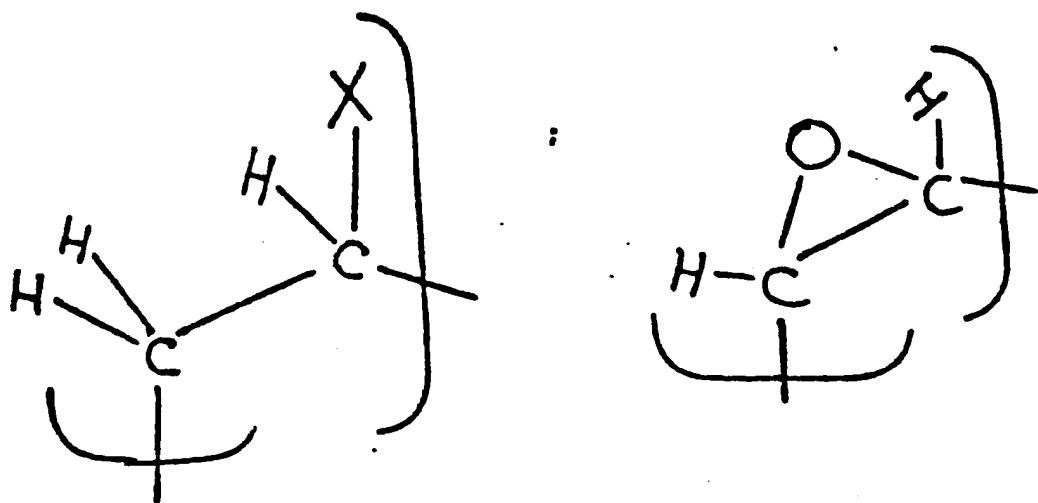
㉚ Substituted tetrahydroindane derivatives and organoleptic uses of substituted tetrahydroindanes.

㉛ A substituted tetrahydroindane defined according to the structure:

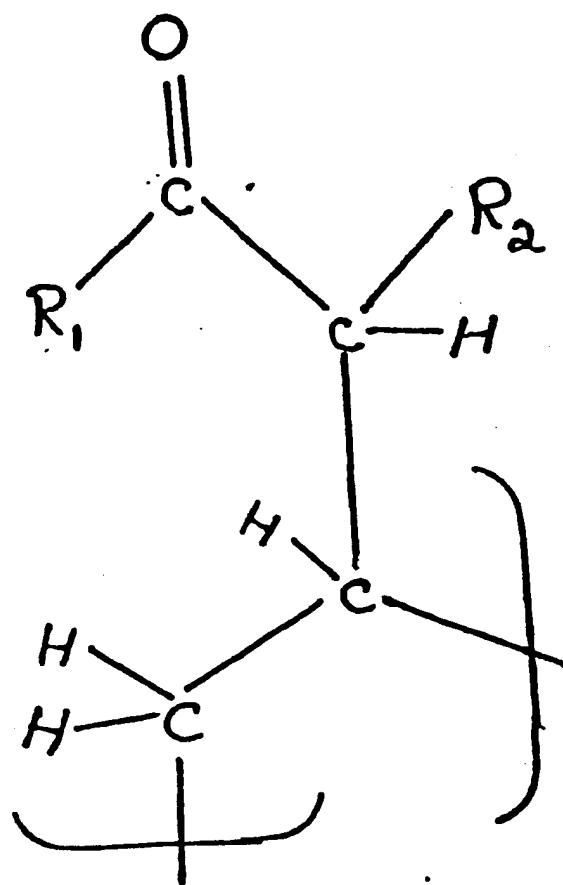


wherein Z is a moiety selected from the group consisting of:

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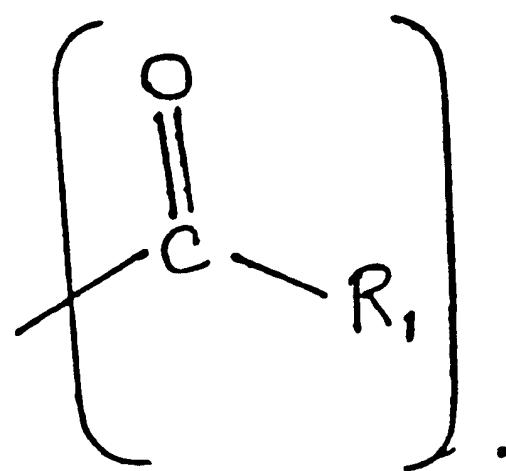
and



wherein X is chloro or bromo; wherein R<sub>1</sub> represents a moiety selected from the group consisting of:  
 $-OR_3$  and  $-O^{\ominus} M$

wherein R<sub>3</sub> is selected from the group consisting of hydrogen, methyl and ethyl; wherein M is alkali metal selected from the group consisting of sodium, potassium and lithium; wherein R<sub>2</sub> is selected from the group consisting of hydrogen and the moiety:

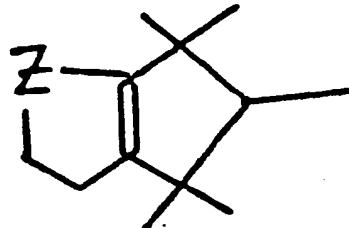
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The instant invention provides substituted tetrahydroindanes defined according to the generic structure:

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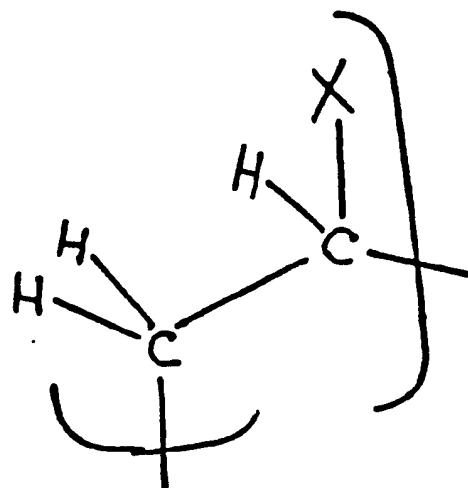
wherein Z represents a moiety selected from the group consisting of

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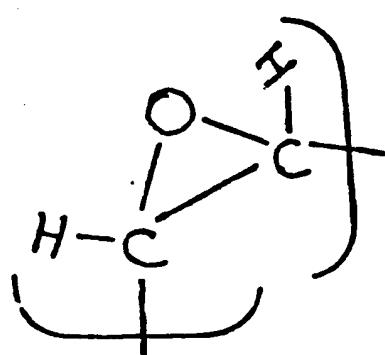
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and

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wherein X represents chloro or bromo; wherein R<sub>1</sub> represents one of the moieties:

35 -OR<sub>3</sub>

or

-O<sup>⊖</sup>M<sup>⊕</sup>

wherein R<sub>3</sub> is hydrogen, methyl or ethyl; wherein M is alkali metal, sodium, potassium or lithium; wherein

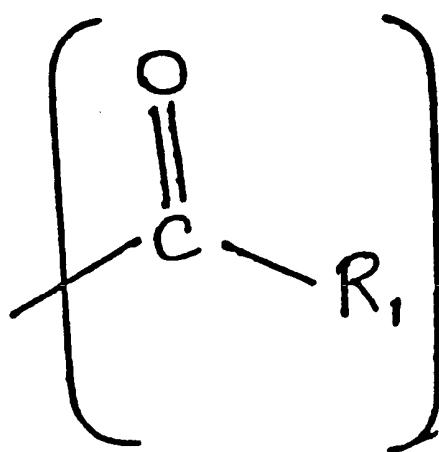
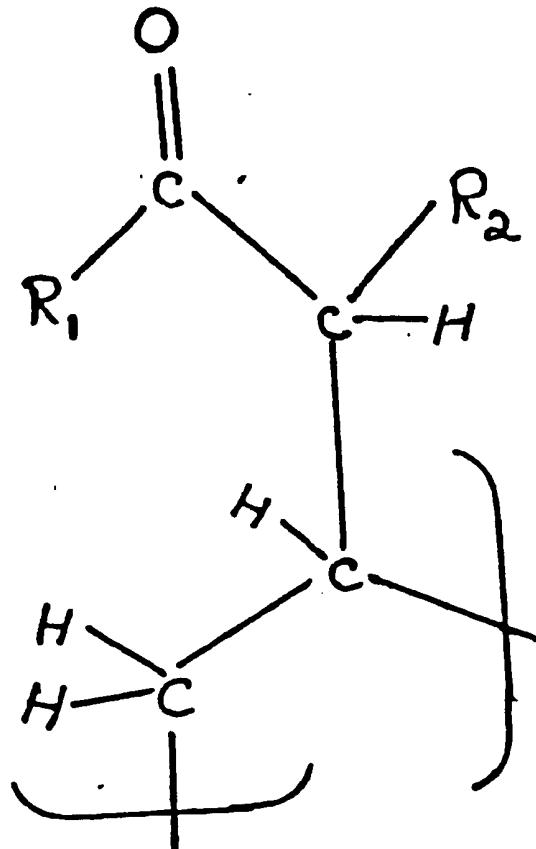
R<sub>2</sub> is hydrogen or the moiety:

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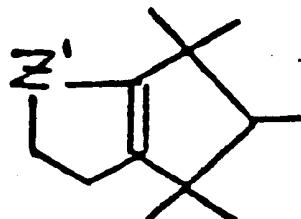
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generic structure:

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are useful in augmenting or enhancing the aroma of perfume compositions, colognes and perfumed articles (including but not limited to solid or liquid anionic, cationic, nonionic or zwitterionic detergents, perfumed polymers, fabric softener compositions and fabric softener articles, cosmetic powders, hair preparations and the like). In the case of substituted tetrahydroindanes useful in augmenting or enhancing the aroma of perfume compositions, colognes and perfumed articles, Z' is a moiety selected from the group consisting of:

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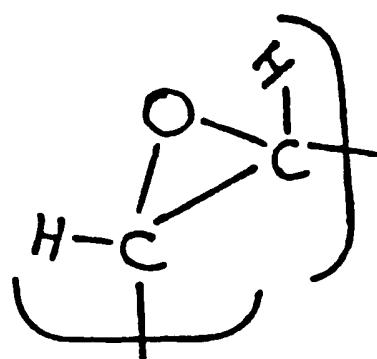
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and

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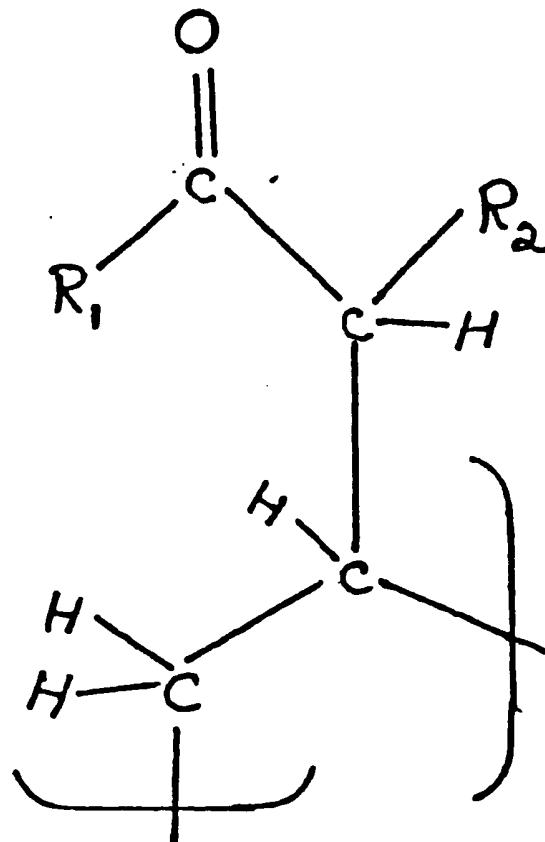
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and wherein R<sub>2</sub> is hydrogen and R<sub>1</sub> is the moiety:

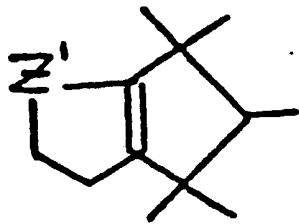
-OR<sub>3</sub>

50 wherein R<sub>3</sub> is methyl or ethyl.

The other of the substituted tetrahydroindanes of our invention are useful as intermediates in synthesis processes for producing compounds which augment or enhance the aroma of perfume compositions, colognes or perfumed articles.

A section of our invention contemplates augmenting or enhancing the aroma of perfume compositions, 55 colognes and perfumed articles as set forth, supra. Thus, the compounds defined according to the generic structure:

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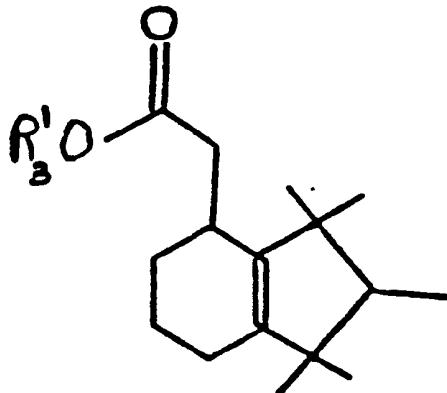


10 which includes the compound having the generic structure:

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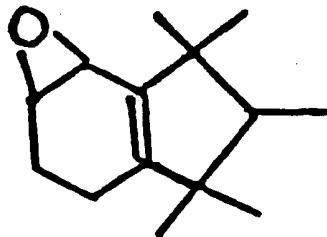
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(wherein R<sub>3'</sub> is methyl or ethyl) as well as the compound having the structure:

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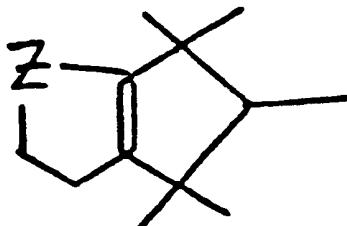


40 augment or enhance dry woody, rose, fruity, floral and tobacco-like aromas with date-like, fig-like, tobacco and rose topnotes.

The compounds of our invention defined according to the generic structure:

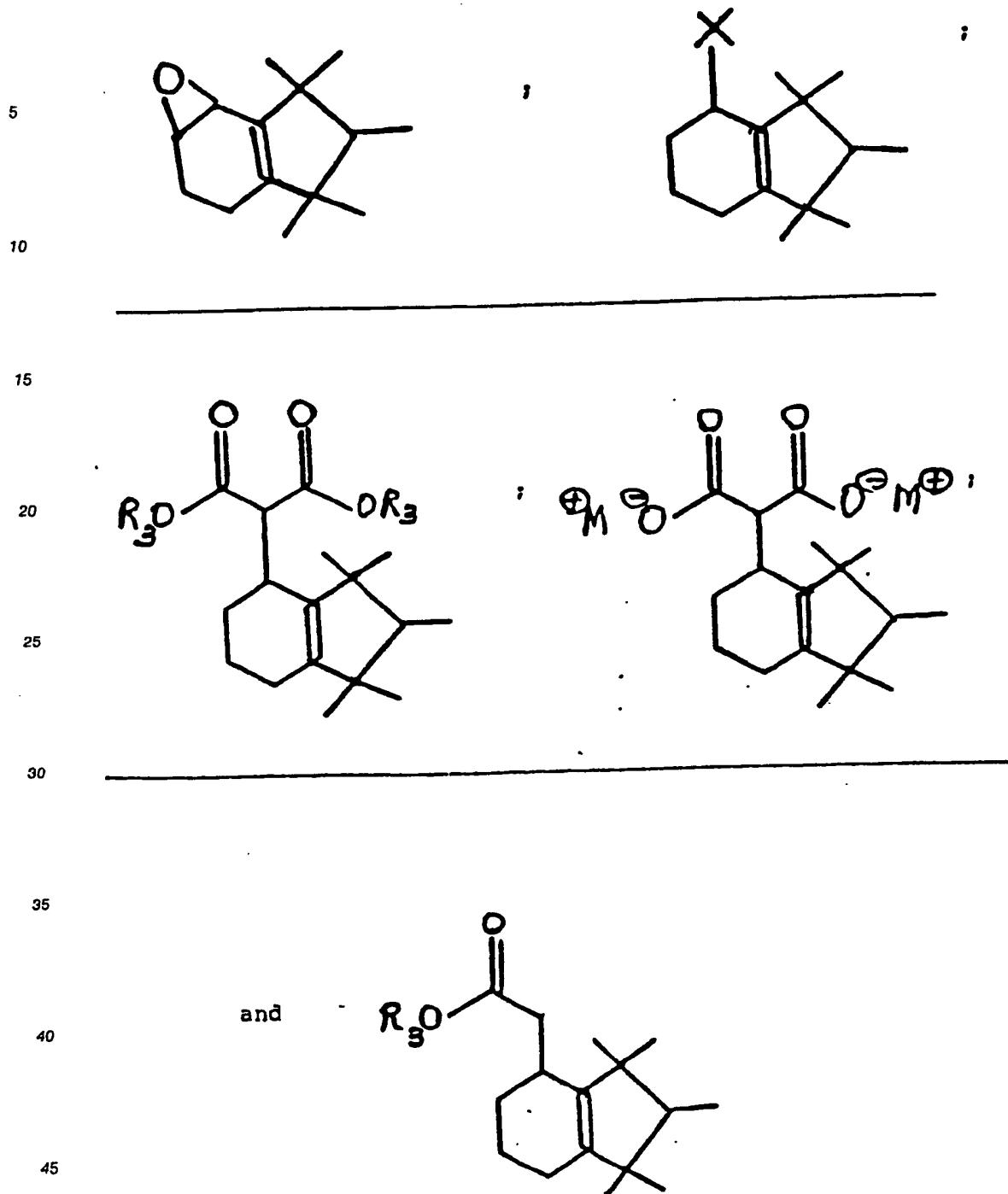
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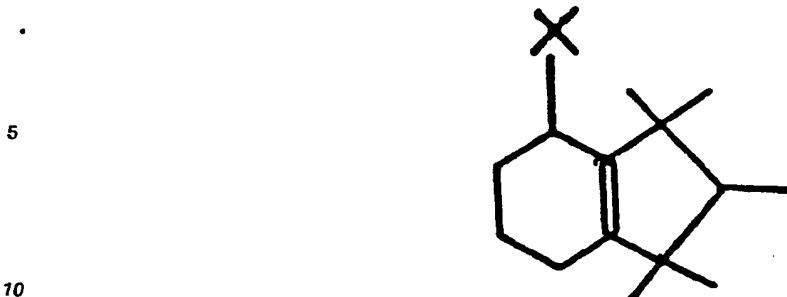


wherein Z is defined, supra, include compounds having the following structures:

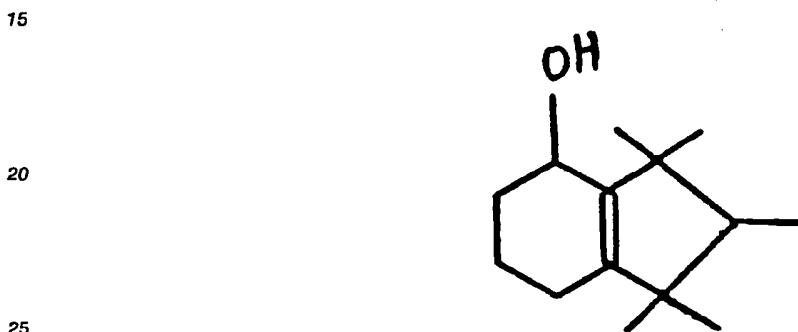
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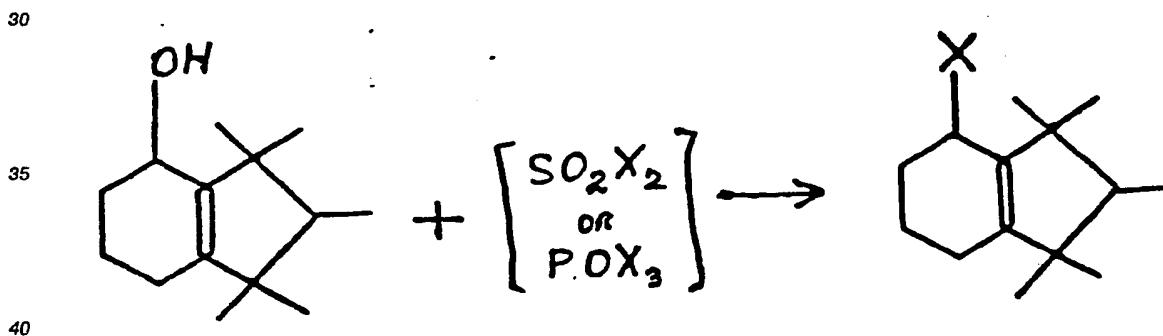
50 The compounds defined according to the structure:



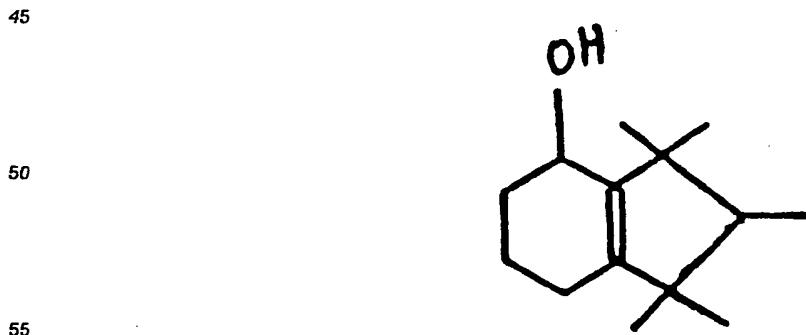
may be prepared by means of reacting the compound having the structure:



with a halogenating agent such as  $\text{SO}_2\text{Cl}_2$ ,  $\text{SO}_2\text{Br}_2$ ,  $\text{POCl}_3$ ,  $\text{POBr}_3$ ,  $\text{PCl}_5$ , nitrosylchloride, N-chlorosuccinimide and the like according to the reaction:



The precursor compound having the structure:



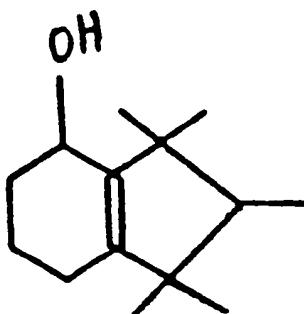
may be prepared according to Example I(c), at column 4, line 71 of U.S. Letters Patent No. 3,636,165

carried out in the presence of an inert solvent such as toluene at temperatures in the range of from about 50 up to about 80 °C with approximately equimolar amounts of halogenating agent and compound having the structure:

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Preferably the reaction is carried out at atmospheric pressure but sub-atmospheric and super-atmospheric pressures may be used. At the end of the reaction, the reaction mass is washed with water and aqueous

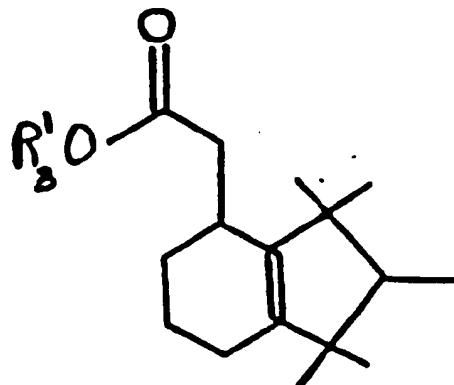
20 base (e.g., aqueous sodium bicarbonate solution). The resulting product is dried and may be used without further purification for subsequent reaction.

In preparing compounds defined according to the generic structure:

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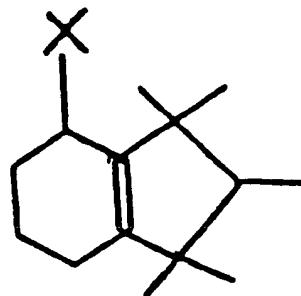
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wherein R<sub>3</sub> is methyl or ethyl (which compounds are useful for their perfumery properties in augmenting or  
40 enhancing the aroma of perfume compositions, colognes or perfumed articles), the compound having the structure:

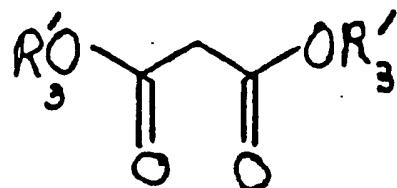
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55 (wherein X is chloro or bromo) is first reacted with a malonic ester defined according to the structure:

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wherein R<sub>3</sub>' represents methyl or ethyl in the presence of an alcoholic solution of an alkali metal alkoxide  
10 such as a 25% solution of sodium methoxide in methanol according to the reaction:

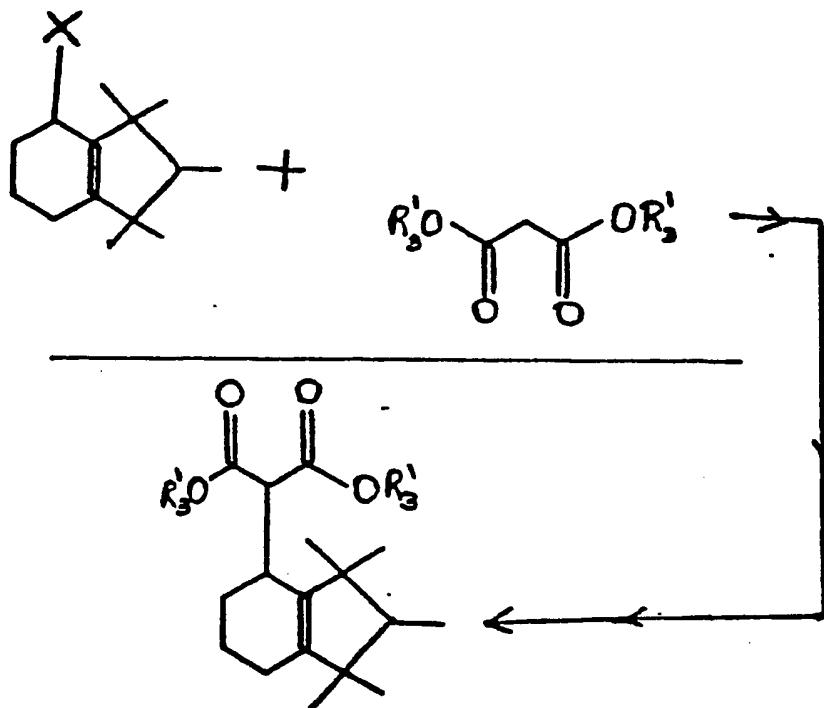
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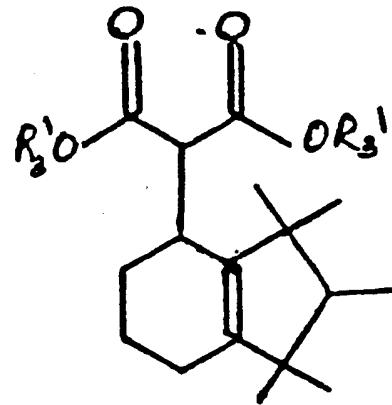
The resulting product having the structure:

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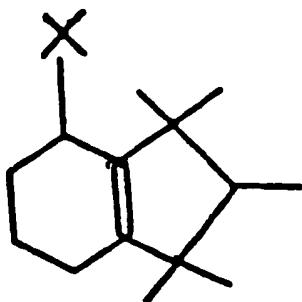
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wherein R<sub>3</sub>' is methyl or ethyl is a novel chemical intermediate.

The reaction preferably takes place at ambient conditions, e.g., 20-30 °C at atmospheric pressure.  
Preferably, the mole ratio of alkali metal alkoxide:malonic ester:compound having the structure:

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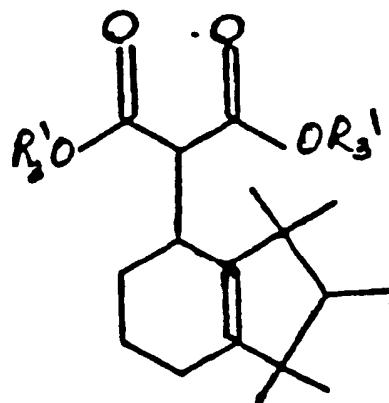
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is approximately 1:1:1.

The resulting product having the structure:

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is then saponified using aqueous base, e.g., an aqueous solution of the compound having the structure:

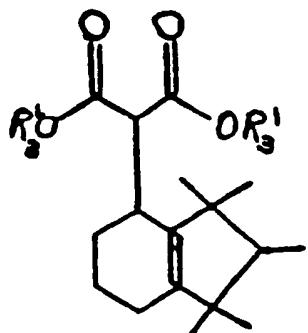
MOH

wherein M is sodium, potassium or lithium according to the reaction:

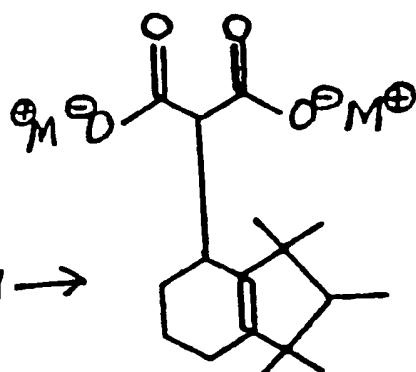
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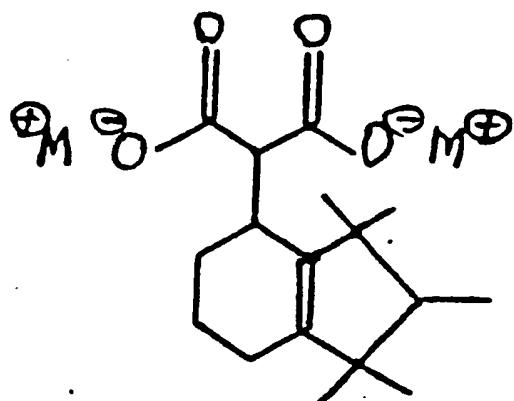
+ MOH →



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The resulting compound having the structure:

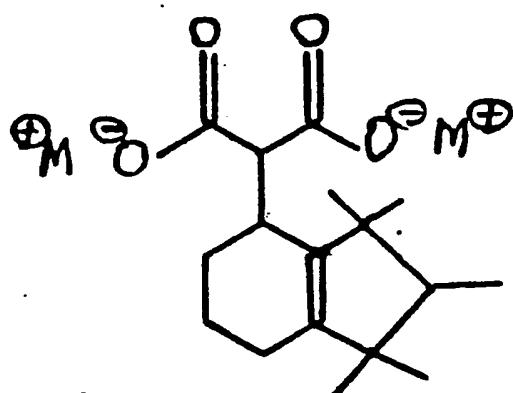
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is a novel reaction intermediate. The saponification reaction takes place at reflux conditions over a period of between about one and about five hours.

The resulting salt having the structure:

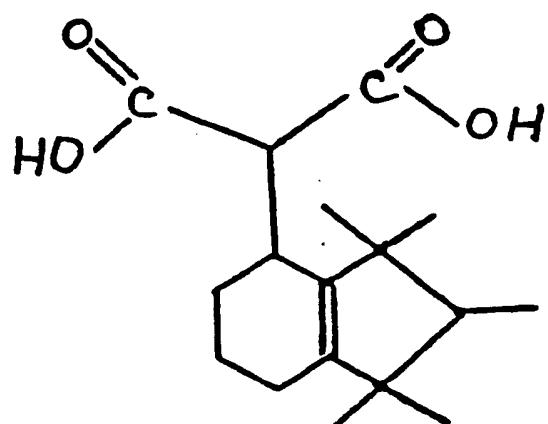
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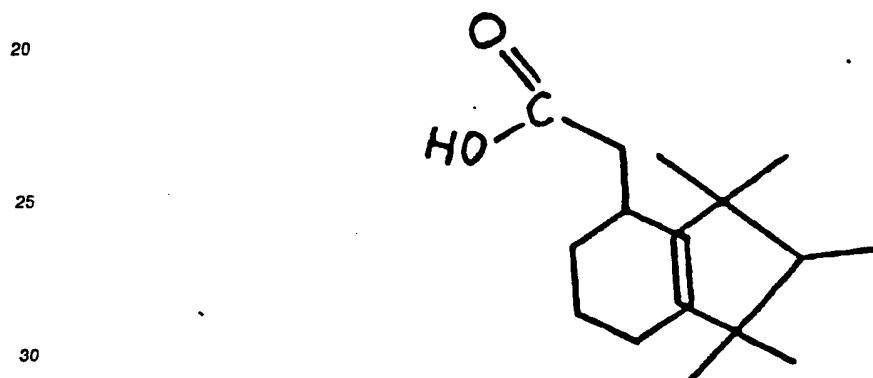
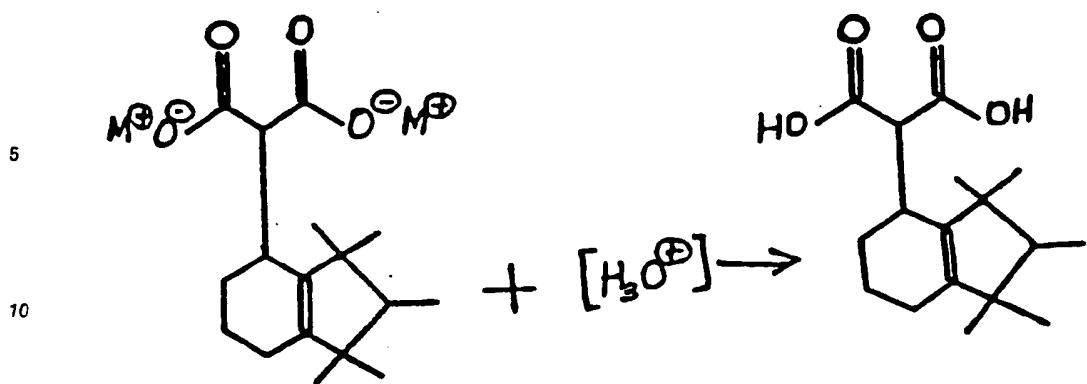
is then treated with mineral acid such as hydrochloric acid or sulfuric acid in order to form the dicarboxylic acid having the structure:

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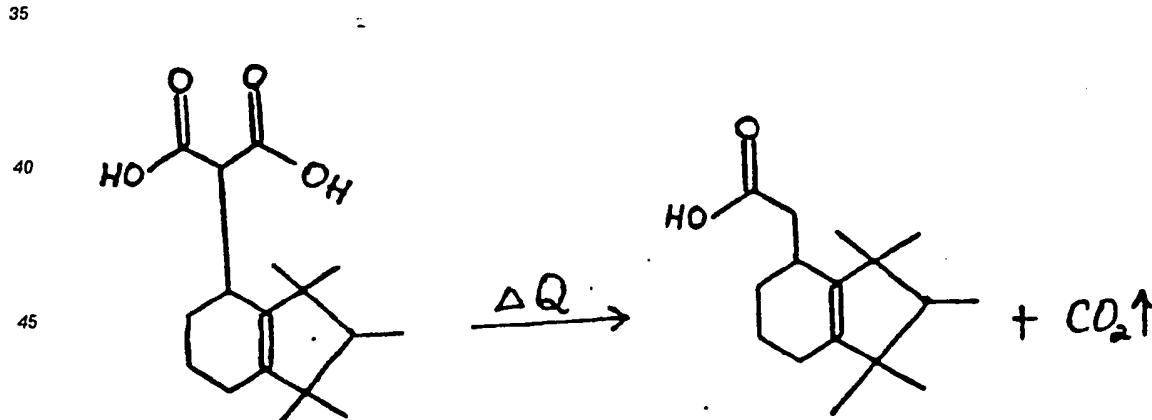


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a novel chemical intermediate according to the reaction:



according to the reaction:



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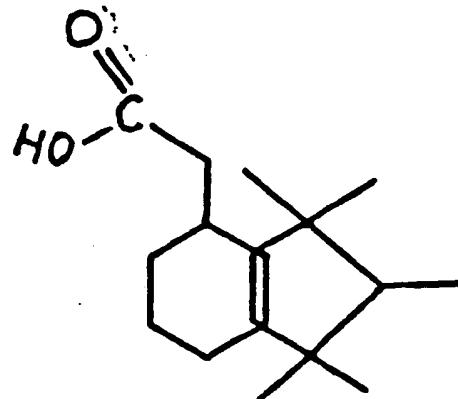
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is a novel chemical intermediate.  
The compound having the structure:

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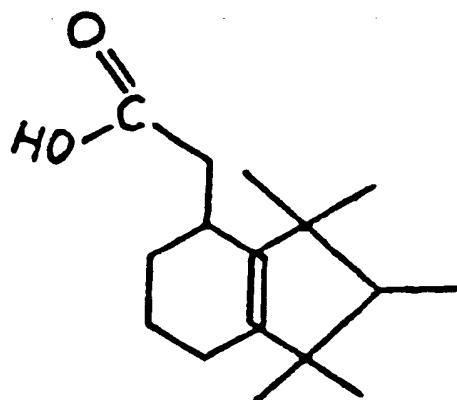


35 is then esterified using standard methyl or ethyl esterification conditions; for example, refluxing the compound having the structure:

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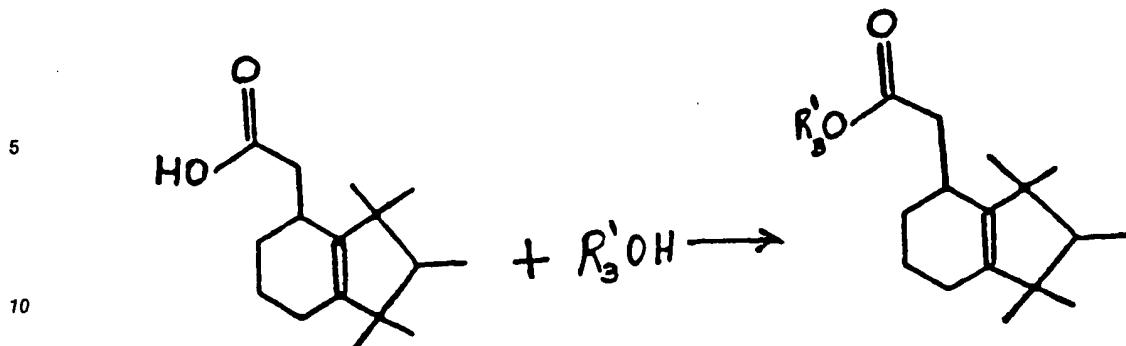
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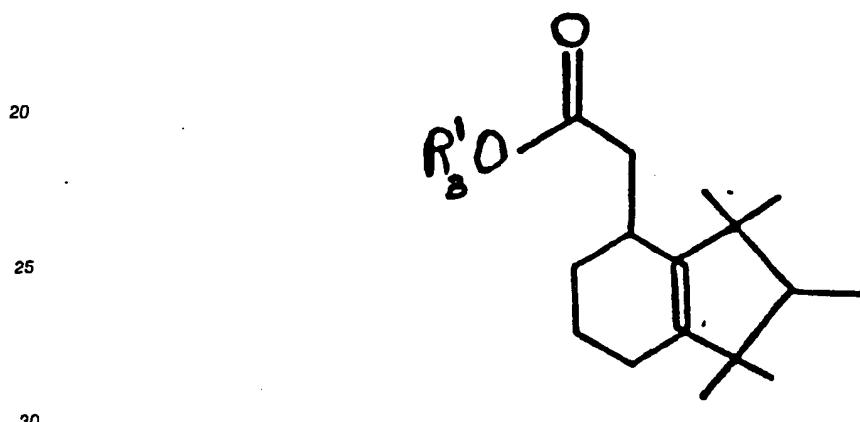
with methanol or ethanol in the presence of concentrated sulfuric acid in accordance with the reaction:

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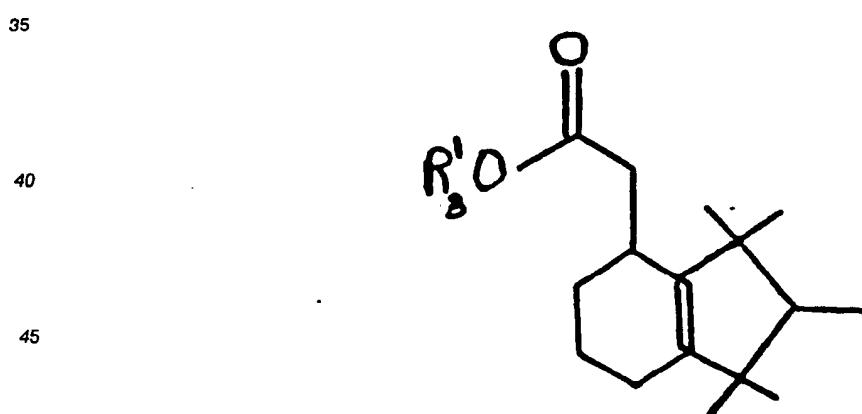
wherein  $R_3'$  is methyl or ethyl.

15 The compound having the structure:



is a valuable perfumery material having properties as set forth in Table I, infra.

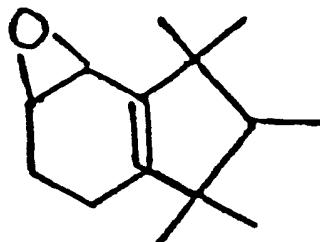
The compound having the structure:



50 is recovered by means of fractional distillation.

The compound having the structure:

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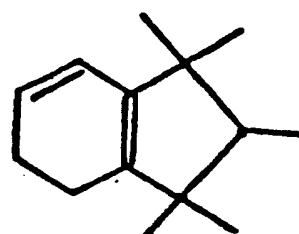


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useful for its organoleptic properties in augmenting or enhancing the aroma of perfume compositions, colognes or perfumed articles is prepared by epoxidation of the compound having the structure:

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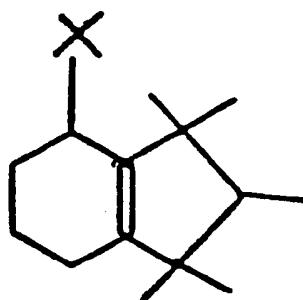


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which, in turn, may be prepared by dehydrohalogenation of the compound having the structure:

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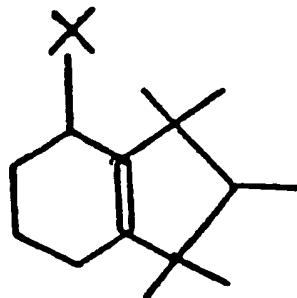
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or in the alternative it may be prepared according to Example II(b) to be at line 50 of column 5 of U.S. Letters Patent No. 3,806,472 issued on April 23, 1974, the specification for which is incorporated herein by reference.

In carrying the dehydrohalogenation of one of the compounds defined according to the structure:

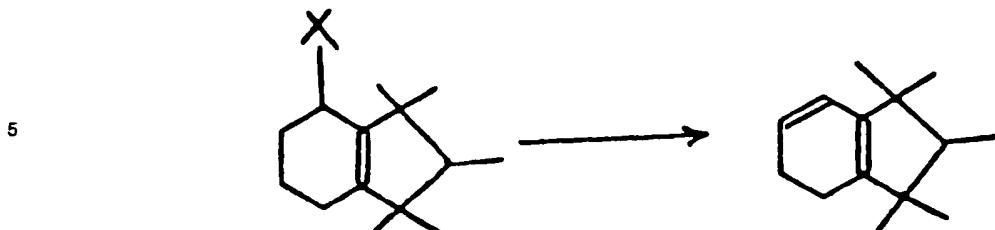
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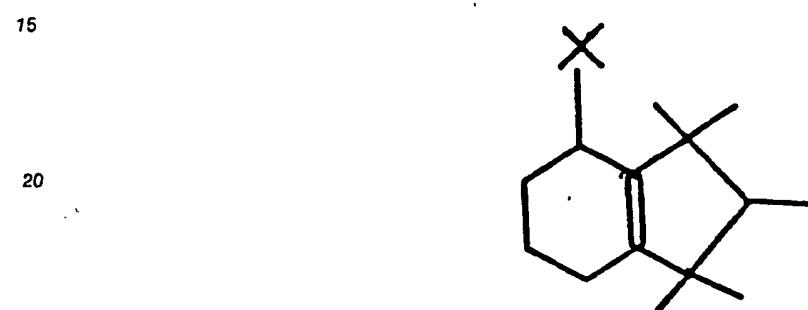


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in accordance with the reaction:

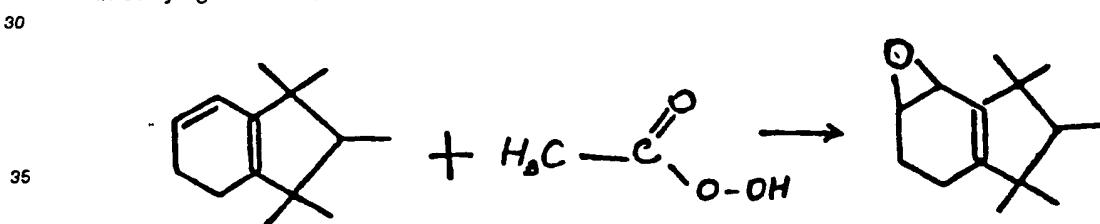


10 standard dehydrohalogenation procedures may be used. Thus, the reaction may be carried out using a tributyl amine dehydrohalogenation reagent at reflux conditions for a period of between about one and about four hours. The mole ratio of dehydrohalogenation reagent:compound having the structure:



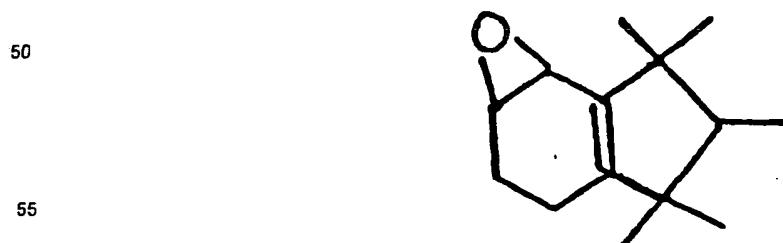
is preferably about 1:1. At the end of the reaction, the reaction mass is cooled and washed with water and weak acid and used without further purification in the epoxidation step.

In carrying out the epoxidation reaction, to wit:



40 (shown using a peracetic acid epoxidation reagent, standard epoxidation reagents may be used, for example, peracetic acid as set forth in the above reaction, perbenzoic acid and the like. The epoxidation reaction is preferably carried out in the presence of an inert solvent such as toluene at a temperature in the range of from about 30 °C up to about 50 °C with the mole ratio of epoxidation reagent:hydrocarbon being preferably about 1:1. The reaction is carried out in the presence of a small amount of weak base such as sodium carbonate. At the end of the reaction, the reaction mass is quenched with water and the organic layer is washed with weak base, e.g., 5% sodium carbonate. The reaction mass is then fractionally distilled to yield the organoleptically useful compound having the structure:

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The following Table I sets forth examples of two of the substituted tetrahydroindanes useful in augmenting or enhancing the aroma of perfume compositions, perfumed articles and colognes and their organoleptic properties:

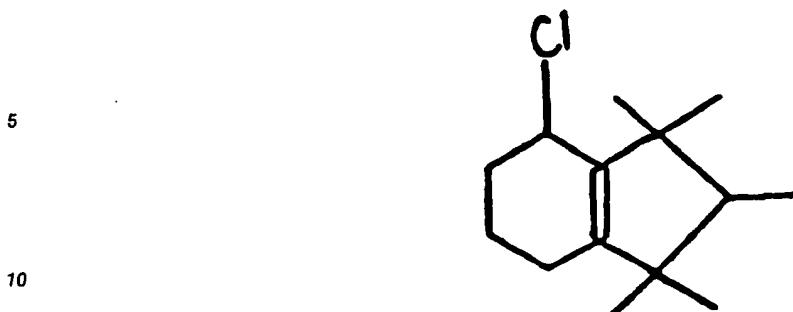
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<u>TABLE I</u>		
10	<u>Structure of Substituted Tetrahydroindane Derivatives</u>	<u>Perfumery Properties</u>
15	The compound having the structure:	A dry woody, rose and fruity aroma profile.
20		
25	prepared according to Example II.	
30	The compound having the structure:	A fruity, floral, tobacco-like and rose aroma with date-like, fig-like, tobacco and rose topnotes.
35		
40	prepared according to Example IV.	
45		

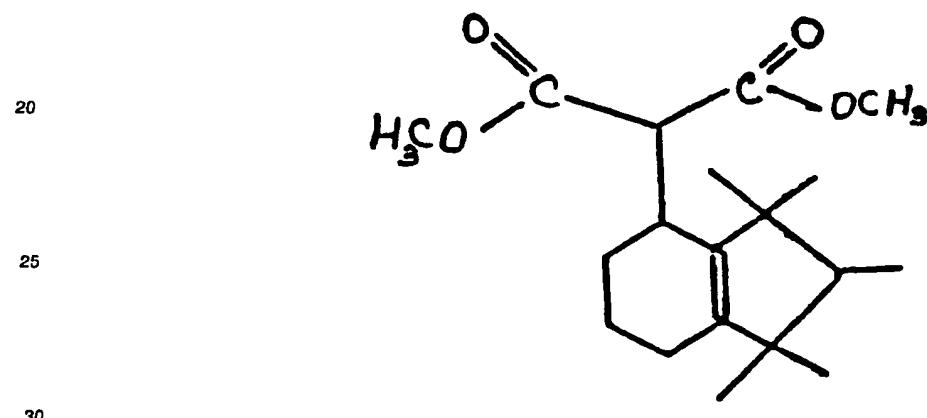
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BRIEF DESCRIPTION OF THE DRAWINGS

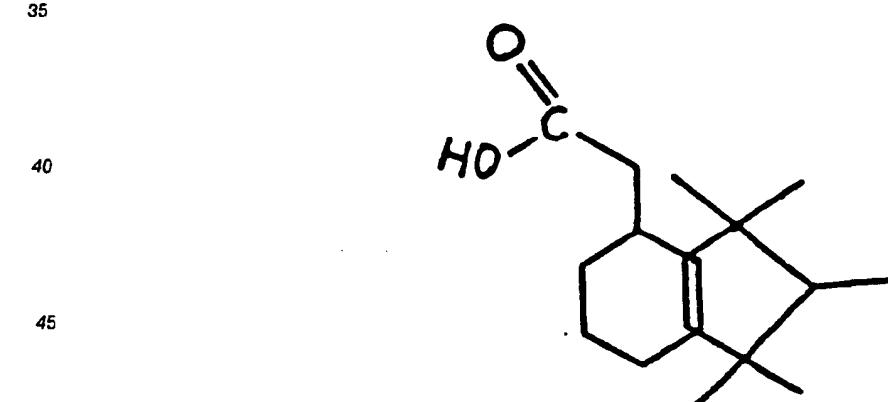
Figure 1 is the GC-MS profile for the compound having the structure:



prepared according to Example I.  
15 Figure 2 is the NMR spectrum for the compound having the structure:

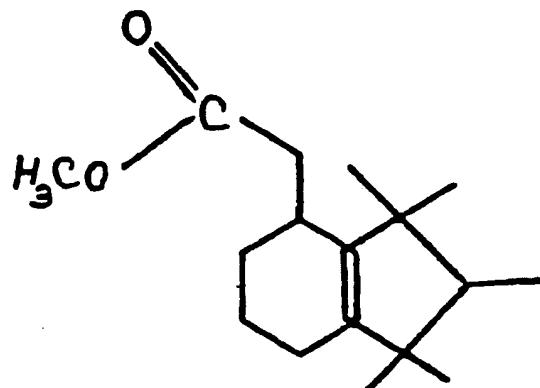


prepared according to Example II.  
35 Figure 3 is the NMR spectrum for the compound having the structure:



50 prepared according to Example II.  
55 Figure 4 is the NMR spectrum for the compound having the structure:

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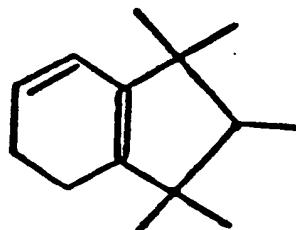
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prepared according to Example II.

Figure 5 is the NMR spectrum for the compound having the structure:

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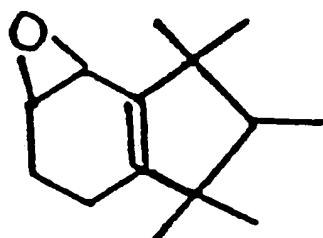
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30 prepared according to Example III.

Figure 6 is the NMR spectrum for the compound having the structure:

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prepared according to Example IV.

45 Figure 7 is a partial side elevation and partial sectional view of an apparatus for forming polymer pellets scented with one of the perfume compositions or perfumery materials of our invention.

Figure 8 is a section taken on line 8-8 of Figure 7.

#### DETAILED DESCRIPTION OF THE DRAWINGS

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Referring to Figures 7 and 8, the apparatus used in producing polymeric fragrances containing the substituted tetrahydroindanes of our invention comprises a device for forming scented polyolefin (for example) pellets which comprises a vat or container 212 into which a mixture of polyolefins such as polyethylene or an aromatic substance or scented material containing or consisting of at least one of the 55 substituted tetrahydroindanes of our invention is placed. The container is closed by an air tight lid 228, and clamped to the container by bolts 265. A stirrer 273 traverses the lid or cover 228 in air tight manner and is rotated in a suitable manner. A surrounding cylinder 212 having heating coils 212A which are supplied with

inside the container 212 such that polyethylene or other thermoplastic polymer in the container will be maintained in the molten or liquid state. It has been found advantageous to employ a colorless, odorless polymer (e.g., polyethylene) with a viscosity ranging between 180 and 220 Saybolt seconds and having a melting point in the range of 200-280° F. The heater is operated to maintain the upper portion of the 5 container 212 within a temperature range of from 250-350° F. The bottom portion of the container is heated by means of heating coils 212A heated through a control connected thereto through a connecting wire 226 to maintain the lower portion of the container within a temperature range of from 250-350° F.

Thus, polymer (e.g., polyolefin) added to the container 212 is heated from 10-12 hours whereafter a scent or aroma imparting material which contains or consists of at least one of the substituted tetrahydroindanes of our invention is quickly added to the melt. The material must be compatible with the polyolefin and forms a homogeneous liquid melt therewith. The scented material containing at least one of the substituted tetrahydroindanes of our invention is of a type for the particular aroma desired and formulated specifically for the scenting purpose for which the polyolefin will be employed. The heat resisting coils and aromatic materials in some instances in solid or powdered form may be employed and added to the 10 polyolefin in the container 212. Generally, about 10-30% by weight of scenting material is added to the polyolefin.

After the scent imparting material containing or consisting of at least one of the substituted tetrahydroindanes of our invention is added to the container 212, the mixture is stirred for a few minutes, for example, 15-15 minutes and maintained within the temperature ranges indicated previously by the heating coils 212A and 218. The controls 216 and 220 are connected through cables 224 and 226 to a suitable supply of 20 electric current for supplying the power for heating purposes.

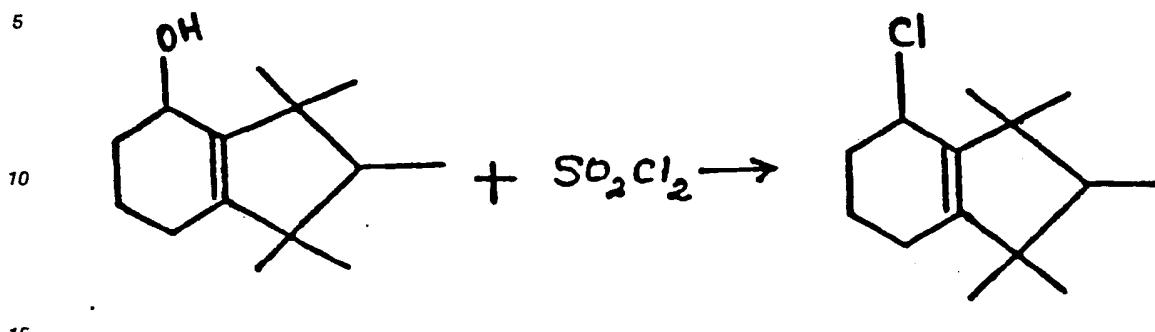
Thereafter, the valve "V" is opened permitting the mass to flow outwardly through conduit 232 having a multiplicity of orifices 234 adjacent to the lower side thereof. The outer end of the conduit 232 is closed so that the liquid polymer (e.g., polyolefin) and aroma imparting mixture (containing at least one of the 25 substituted tetrahydroindanes of our invention) will continuously drop through orifices 234 downwardly from the conduit 232. During this time, the temperature of the polymer (e.g., polyolefin) and aroma mixture containing or consisting of at least one of the substituted tetrahydroindanes of our invention in the container 212 is accurately controlled so that a temperature in the range of from about 210-275° F will exist in the 30 conduit 232. The regulation of the temperature through the control 216 and the control 220 is essential in order to insure temperature balance to provide for the continuous dropping or dripping of molten polymer (e.g., polyolefin) and scenting material containing at least one of the substituted tetrahydroindanes of our invention through the orifices 234 at a rate which will insure the formation of droplets 236 which will fall downwardly onto a moving conveyor belt 238 trained to run between conveyor wheels 240 and 242 beneath the conduit 232.

When the droplets 236 fall onto the conveyor 238, they form pellets 244 which harden almost 35 instantaneously and fall off the end of the conveyor 238 into a container 259 which is advantageously filled with water or some other suitable cooling liquid in order to insure the rapid cooling of each of the pellets. The pellets 244 are then collected from the container 259 and utilized in a process as illustrated, infra.

A feature of this aspect of the process of our invention is in the provision for moistening the conveyor 40 belt 238 to insure rapid formation of the solid polymer (e.g., polyolefin) scented pellets 244 without sticking to the belt. The belt 238 is advantageously of a material which will not normally stick to a melted plastic but the moistening means 248 insures a sufficiently cold temperature of the belt surface for the adequate formation of the pellets 244. The moistening means comprises a container 259 which is continuously fed with water 252 to maintain a level 254 for moistening a sponge element 256 which bears against the 45 exterior surface of the belt 238.

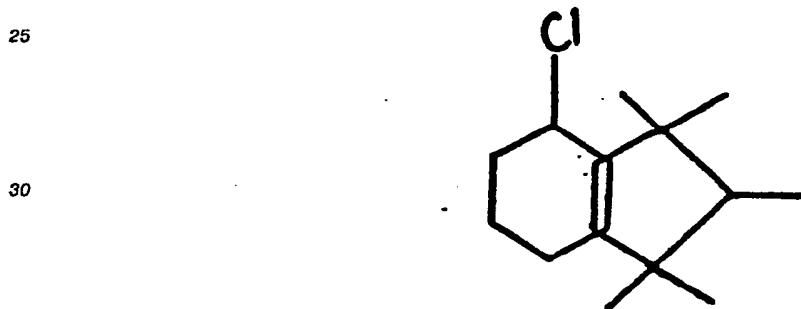
#### EXAMPLE !

### **Reaction:**



A solution of 208 grams of 4,5,6,7-tetrahydro-1-hydroxy-1,1,2,3,3-pentamethylindane in 300 grams of toluene is heated to 70 °C. Thionylchloride (148.5 grams) is added dropwise at 70 °C over a period of one hour. The solution is heated to reflux eliminating SO<sub>2</sub> and HCl gas. The reaction mixture is cooled to 30 °C where upon it is washed with water and then 10% sodium bicarbonate. The solution is dried over 3A molecular sieves and used without further purification in Example II.

Figure 1 is the GC-MS profile of the compound having the structure:



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**EXAMPLE 11**

## PREPARATION OF METHYL-4,5,6,7-TETRAHYDRO-1,1,2,3,3-PENTAMETHYL-4-INDANACETATE

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Reactions:

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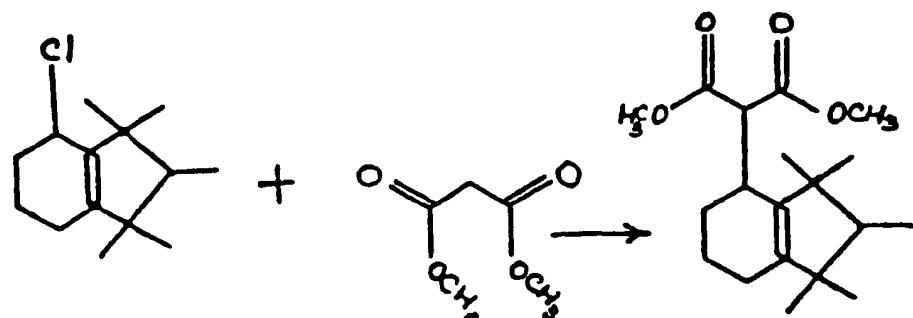
(i)

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(ii)

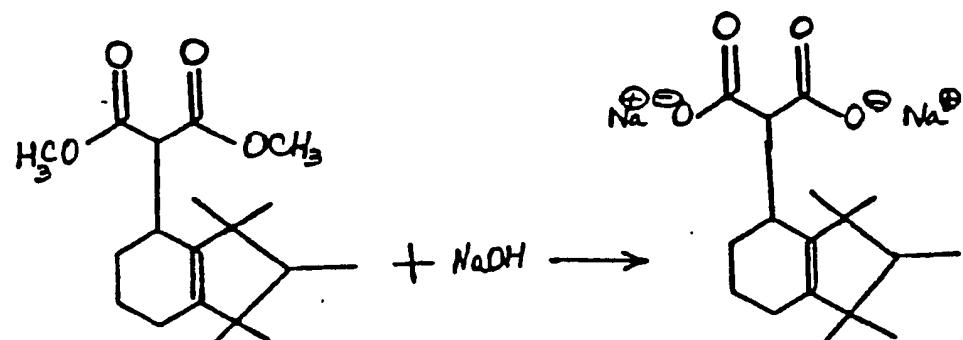
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(iii)

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(iv)

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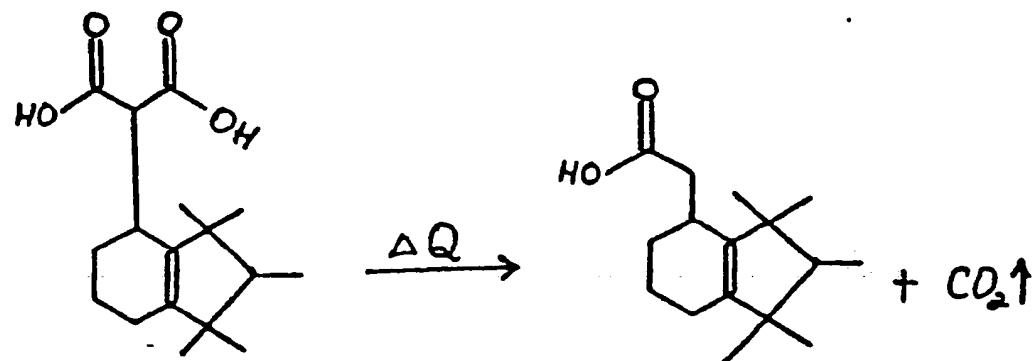
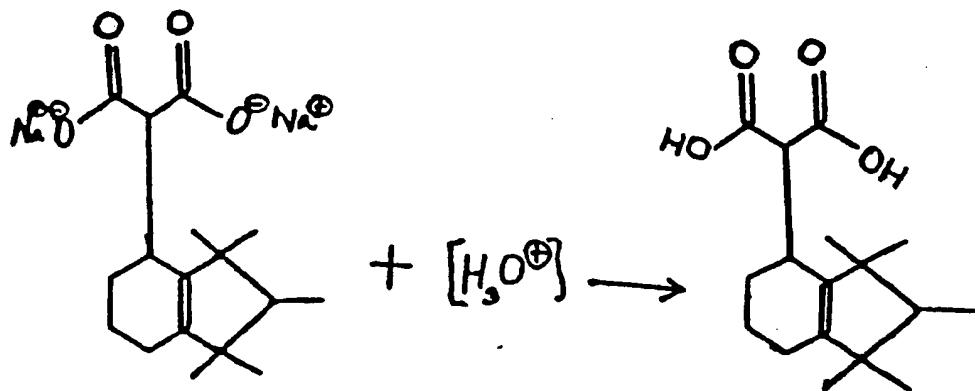
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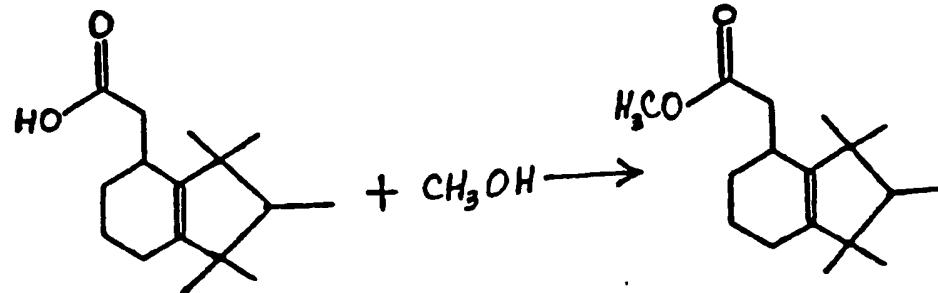
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(v)

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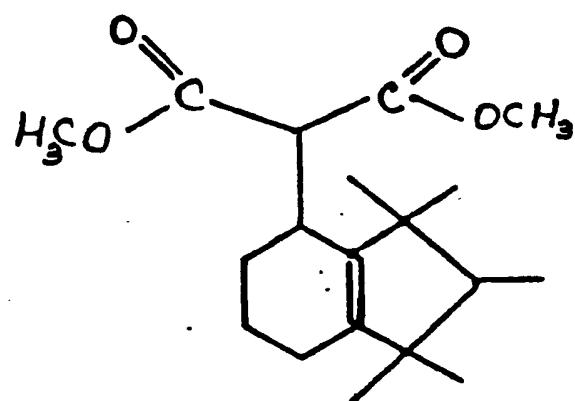
The toluene solution of 4,5,6,7-tetrahydro-1-chloro-1,1,2,3,3-pentamethylindane (100 grams) as prepared in Example I, supra) is added to a solution of 33 grams of dimethylmalonate and 54 grams of 25% sodium methoxide in methanol over a 15 minute period at room temperature. The reaction mass is stirred two hours at room temperature and then poured into 200 ml of water. The resulting organic layer contains the compound having the structure:

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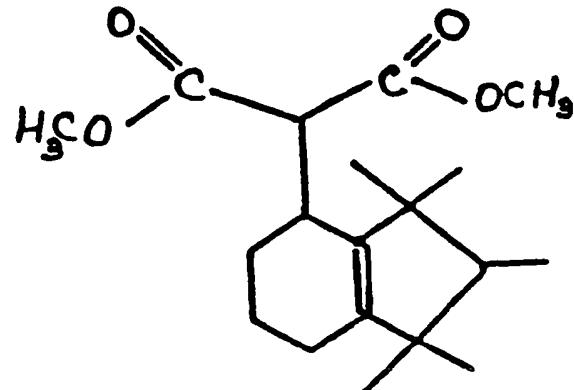
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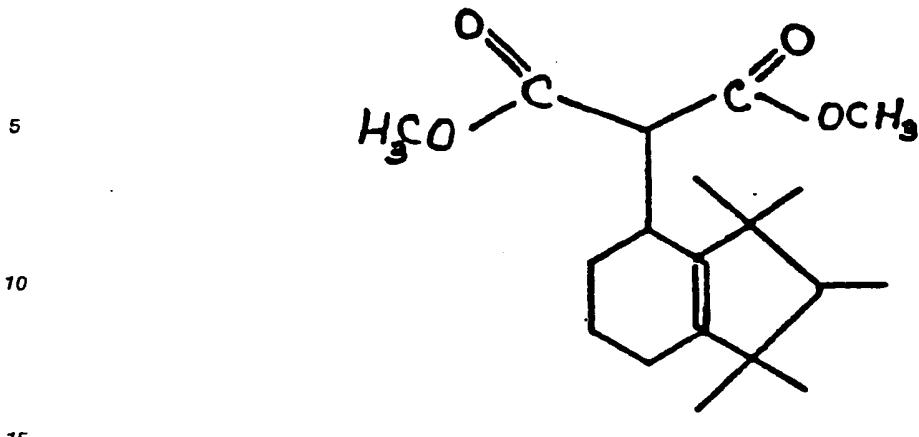
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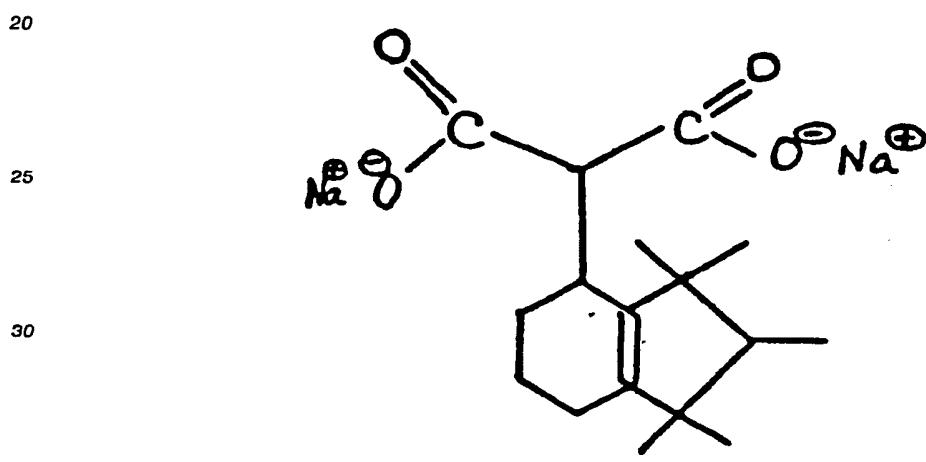
50



The organic layer containing the compound having the structure:



is added to 120 grams of 25% sodium hydroxide at reflux. After heating at reflux for two hours, the mixture is cooled to room temperature. The resulting product has the structure:



Concentrated hydrochloric acid (60 ml) is then added with stirring to effect decarboxylation forming the indanyl acetic acid derivative having the structure:

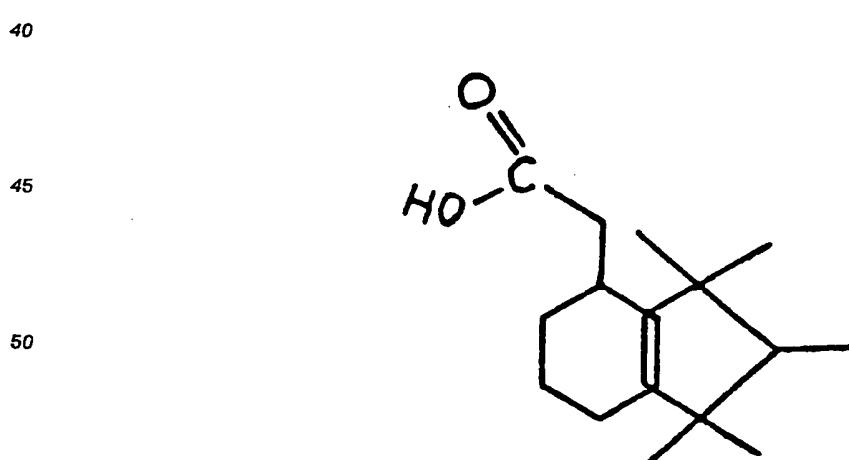
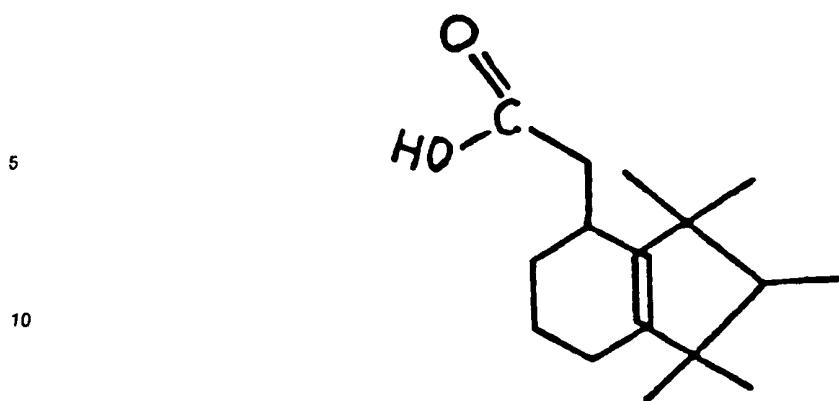


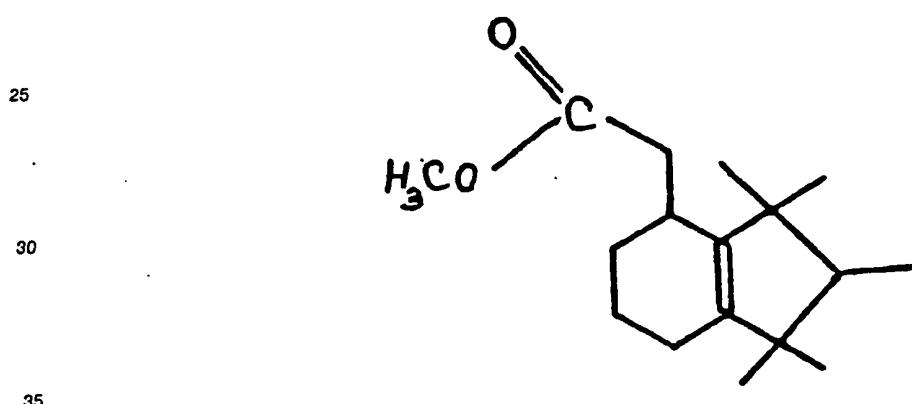
Figure 3 is the NMR spectrum for the compound having the structure:



15      The organic layer is heated for a period of three hours at reflux in 250 ml methanol in the presence of 2 grams of concentrated sulfuric acid. Sodium bicarbonate (6 grams) is added and 200 ml of methanol are removed via atmospheric distillation.

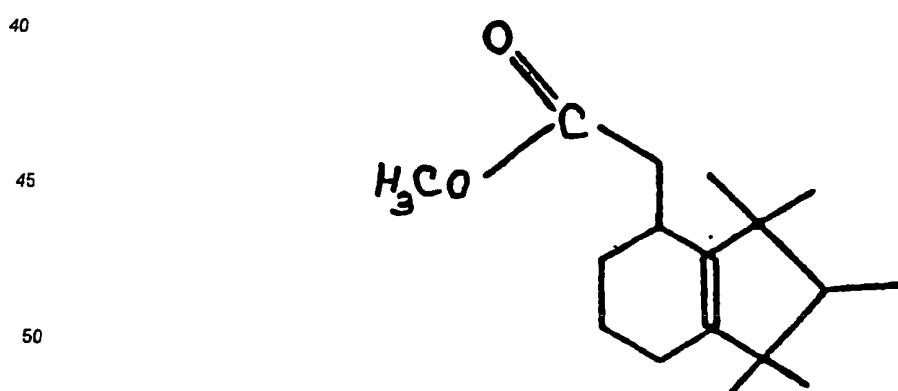
The reaction mass is washed two times with 100 ml 5% sodium bicarbonate solution. Distillation affords

20      28 grams of indanyl compound having the structure:

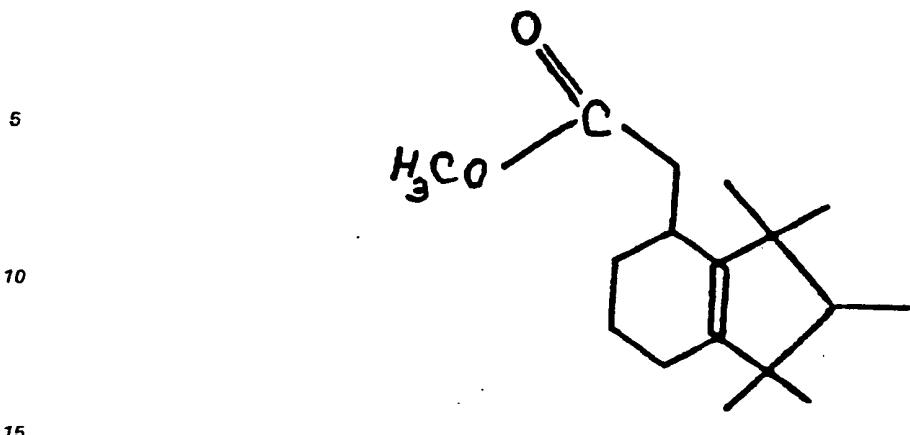


(boiling point 142 °C at 3 mm/Hg. pressure).

Figure 4 is the NMR spectrum for the compound having the structure:



55      The compound having the structure:



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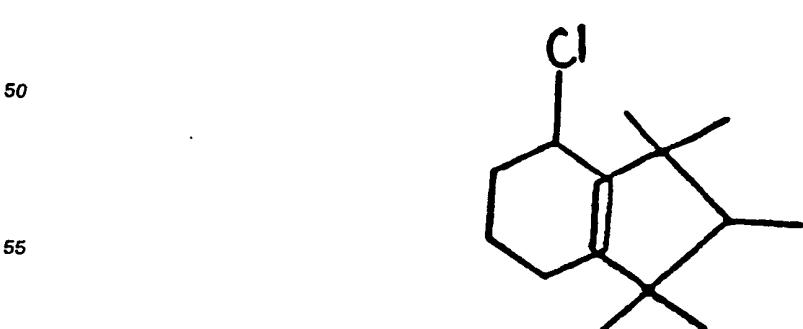
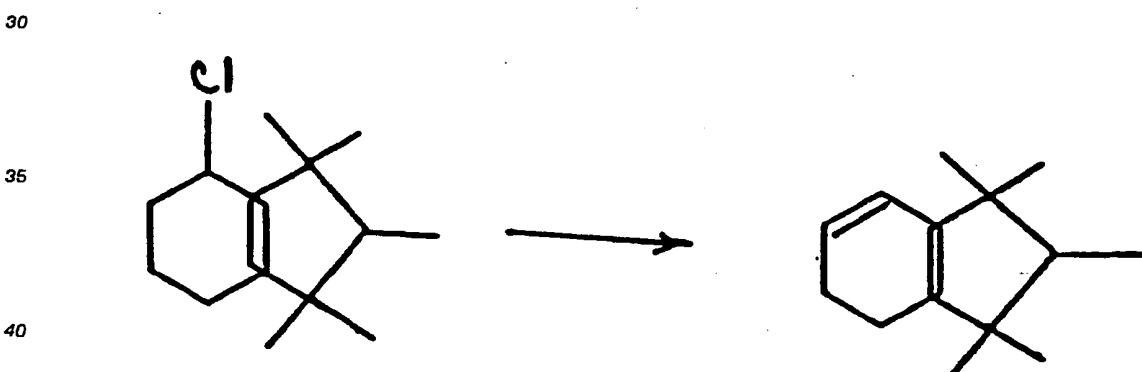
EXAMPLE III

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PREPARATION OF 6,7-DIHYDRO-1,2,3,4,5-PENTAMETHYL INDANE

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Reaction:

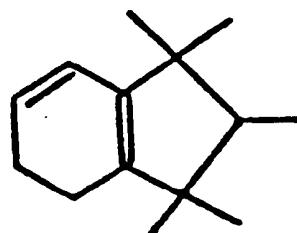


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prepared according to Example I is heated for a period of two hours at reflux in the presence of 110 grams of tributyl amine. The reaction mass is cooled and wash successively with 300 ml water and 300 ml 10% acetic acid. The solution containing the compound having the structure:

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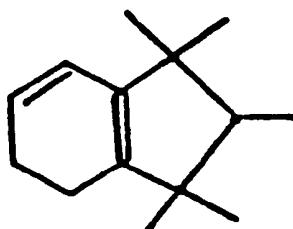


15 is used without further purification in Example IV, infra.

Figure 5 is the NMR spectrum for the compound having the structure:

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EXAMPLE IV

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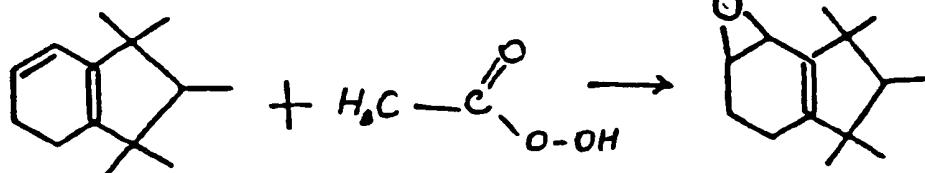
PREPARATION OF 4,5-EPOXY-4,5,6,7-TETRAHYDRO-1,1,2,3,3-PENTAMETHYLINDANE

40

Reaction:

45

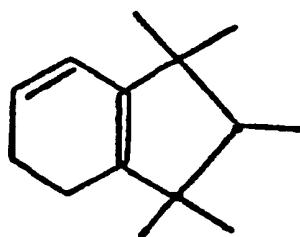
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200 Grams of the toluene solution containing the compound having the structure:

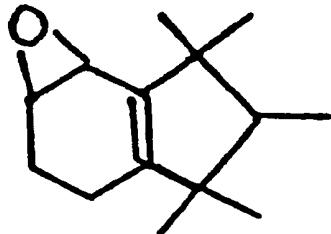
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10 prepared according to Example III is added dropwise over a one hour period to a stirred solution of 5 grams of sodium carbonate in 146 grams of 35% peracetic acid at 40 °C. The reaction mass is stirred at 40 °C for four hours; then poured into 500 ml of water. The resulting organic layer is washed successively with 200 ml of 5% sodium carbonate, 5% sodium bisulfite, and 5% sodium carbonate. Distillation affords 65 grams of the epoxide having the structure:

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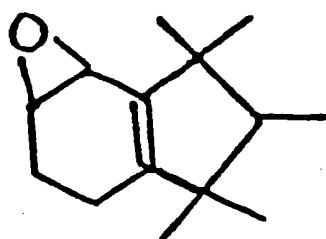


25

(Boiling point: 102 °C at 3 mm/Hg. pressure).

30 The compound having the structure:

35



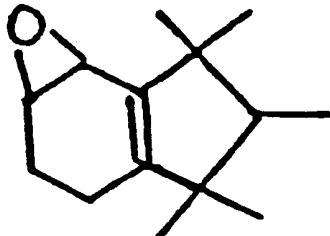
40

has a fruity, floral, tobacco-like and rose aroma with date-like, fig-like, tobacco and rose topnotes.

Figure 6 is the NMR spectrum for the compound having the structure:

45

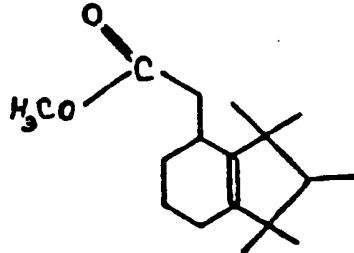
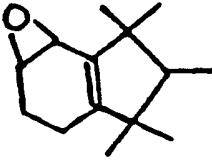
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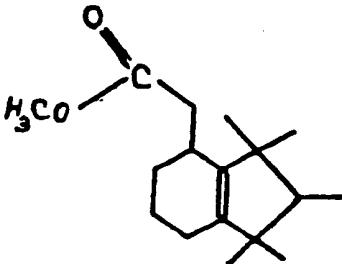
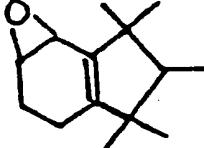


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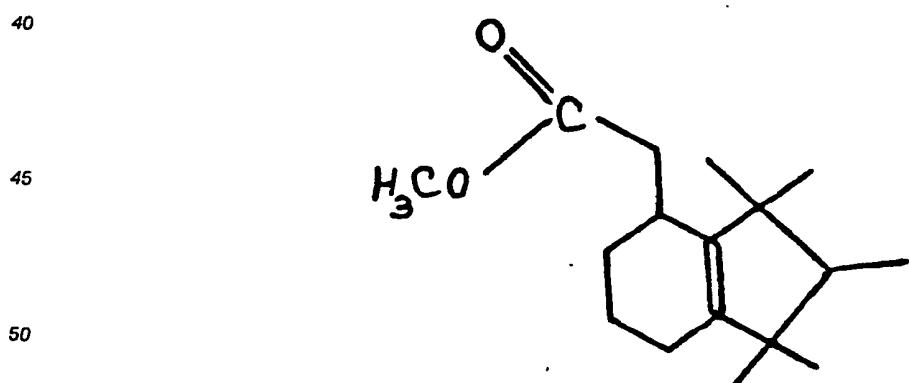
EXAMPLE V

The following rose/tobacco formulations are prepared:

	<u>Ingredients</u>	<u>Parts by Weight</u>		
		V(A)	V(B)	V(C)
5	Phenylethyl alcohol.....	12	12	12
10	Geraniol.....	14	14	14
	Geranyl acetate.....	8	8	8
	Rose oxide.....	4	4	4
15	Bulgarian rose oil.....	0.2	0.2	0.2
	Betadamascenone.....	1	1	1
20	The compound having the structure:			
				
25	prepared according to Example II.			
30		18	0	0
35	The compound having the structure:			
40				
45	prepared according to Example IV.			
50		0	18	0

	<u>Ingredients</u>	<u>Parts by Weight</u>		
		V(A)	V(B)	V(C)
5	50:50 Mixture of the compound having the structure:			
10				
15				
20	prepared according to Example II and the compound having the structure:	0	0	18
25				
30	prepared according to Example IV.			
35				

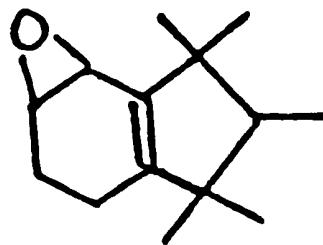
The compound having the structure:



55 prepared according to Example II adds a dry woody and fruity undertone to this rose formulation. Accordingly, the rose formulation of Example V(A) can be described as "rose with a dry woody and fruity undertone".

The compound having the structure:

5

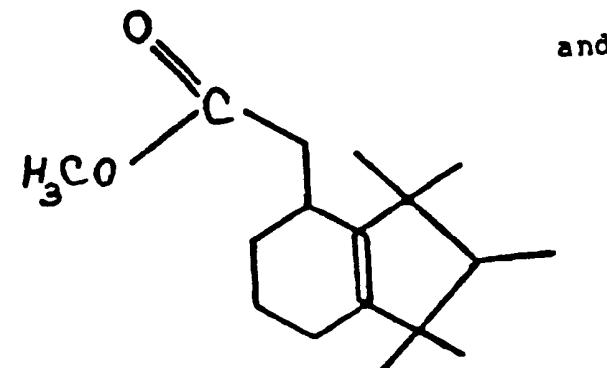


10

prepared according to Example IV adds to this rose formulation a fruity and tobacco-like undertone with date-like, fig-like and tobacco topnotes. Accordingly, the perfume formulation of Example V(B) can be described as "rose with fruity, floral and tobacco-like undertones and date-like, fig-like and tobacco topnotes".

15 The mixture of compounds having the structures:

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of Example V(C) adds to this rose formulation dry woody, fruity, floral and tobacco-like undertones, with date-like, fig-like and tobacco topnotes. Accordingly, the perfume composition of Example V(C) can be described as "rose with dry woody, fruity, floral and tobacco-like undertones and date-like, fig-like and tobacco topnotes".

#### EXAMPLE VI

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#### COSMETIC POWDER PREPARATION

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A cosmetic powder is prepared by mixing in a ball mill 100 grams of talcum powder with 0.25 grams of one of the substances set forth in Table II below containing at least one of the substituted tetrahydroindanes of our invention. Each of the cosmetic powders has an excellent aroma as described in Table II below.

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TABLE II

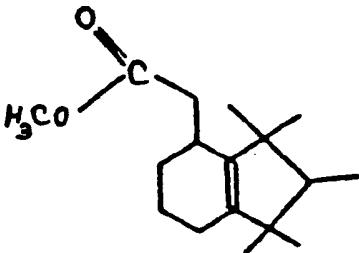
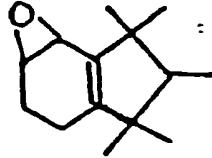
5	<u>Perfumery Substance</u>	<u>Aroma Nuance</u>
10	The compound having the structure:  	A dry woody, rose and fruity aroma profile.
15	prepared according to Example II.	
20	The compound having the structure:  	A fruity, floral, tobacco-like and rose aroma with date-like, fig-like and tobacco and rose topnotes.
25	prepared according to Example IV.	
30		
35		

TABLE II - Cont'd.

40	<u>Perfumery Substance</u>	<u>Aroma Nuance</u>
45	Perfume composition of Example V(A).	Rose with a dry woody and fruity undertone.
50	Perfume composition of Example V(B).	Rose with fruity, floral and tobacco-like undertones and date-like, fig-like and tobacco topnotes.
55	Perfume composition of Example V(C).	Rose with dry woody, fruity, floral and tobacco-like undertones and date-like, fig-like and tobacco topnotes.

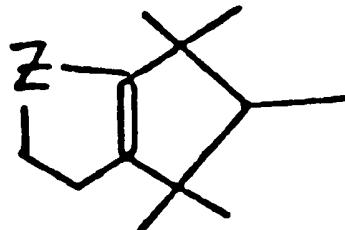
55 The features disclosed in the foregoing description, in the following claims and/or in the accompanying drawings may, both separately and in any combination thereof, be material for realising the invention in diverse forms thereof.

**Claims**

1. A substituted tetrahydroindane defined according to the structure:

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wherein Z is a moiety selected from the group consisting of:

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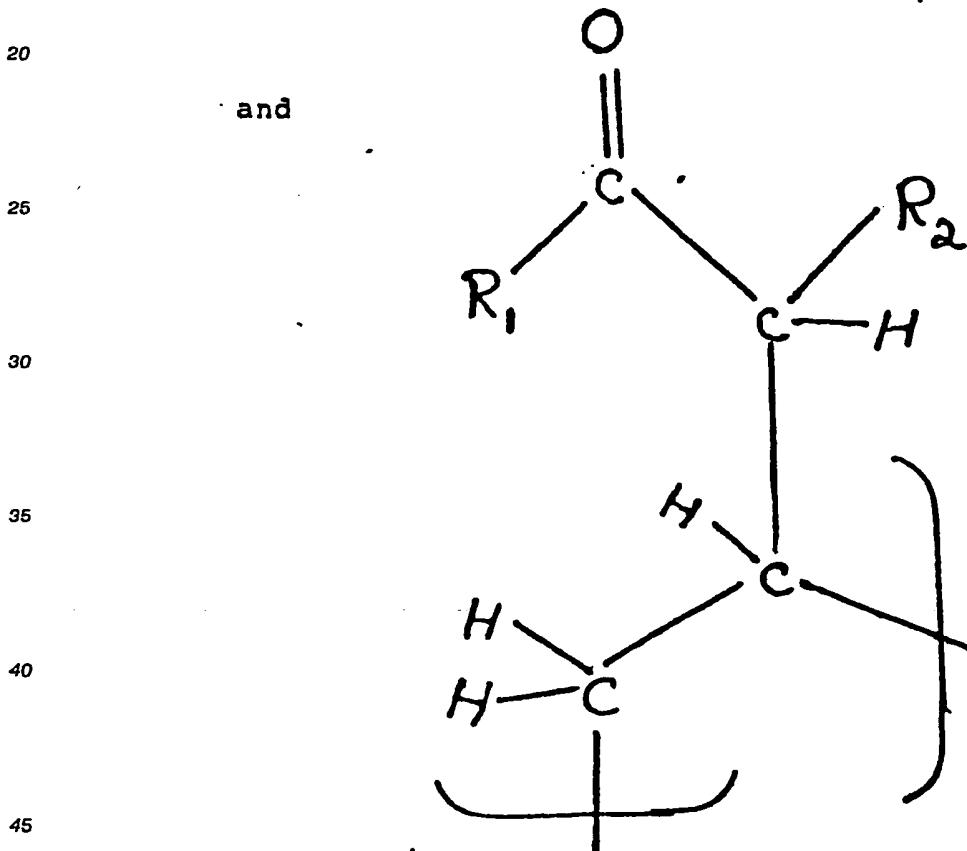
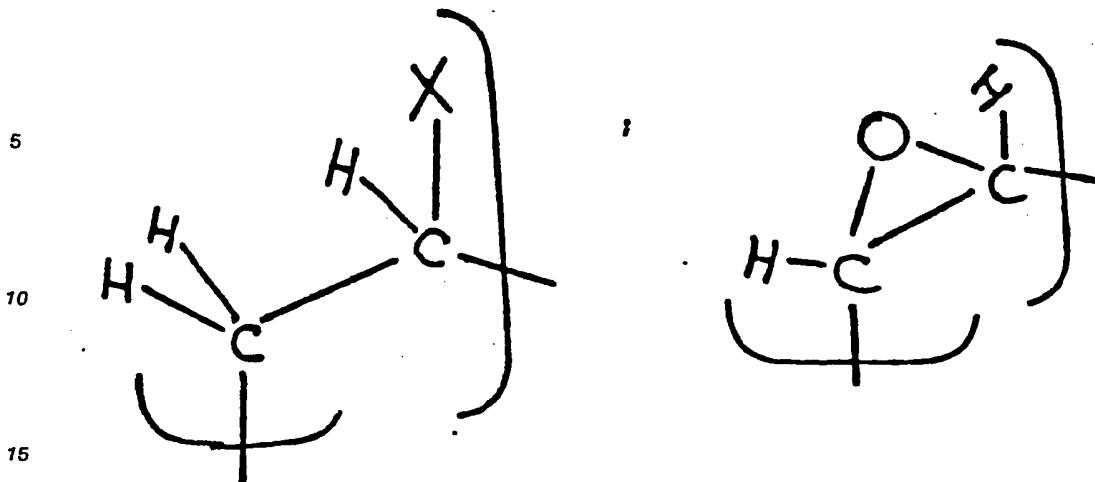
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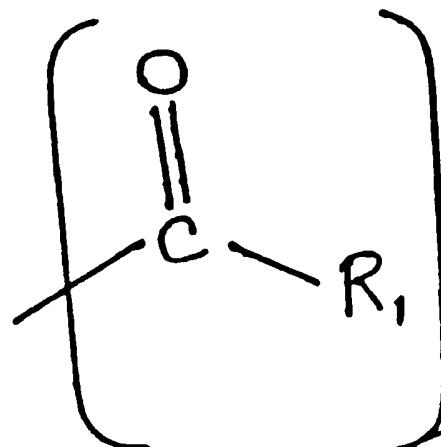
wherein X is chloro or bromo; wherein R<sub>1</sub> represents a moiety selected from the group consisting of:  
-OR<sub>3</sub> and -O<sup>⊖</sup>M<sup>⊕</sup>;

50 wherein R<sub>3</sub> is selected from the group consisting of hydrogen, methyl and ethyl; wherein M is alkali metal selected from the group consisting of sodium, potassium and lithium; wherein R<sub>2</sub> is selected from the group consisting of hydrogen and the moiety:

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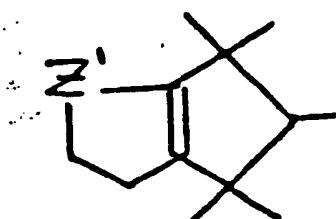
15



2. The substituted tetrahydroindane of Claim 1 having the structure:

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wherein Z' is a moiety selected from the group consisting of:

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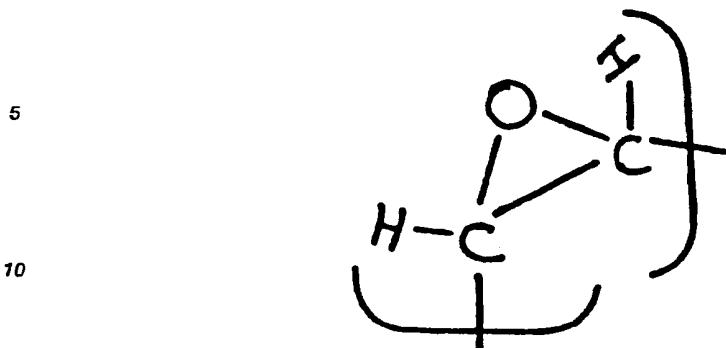
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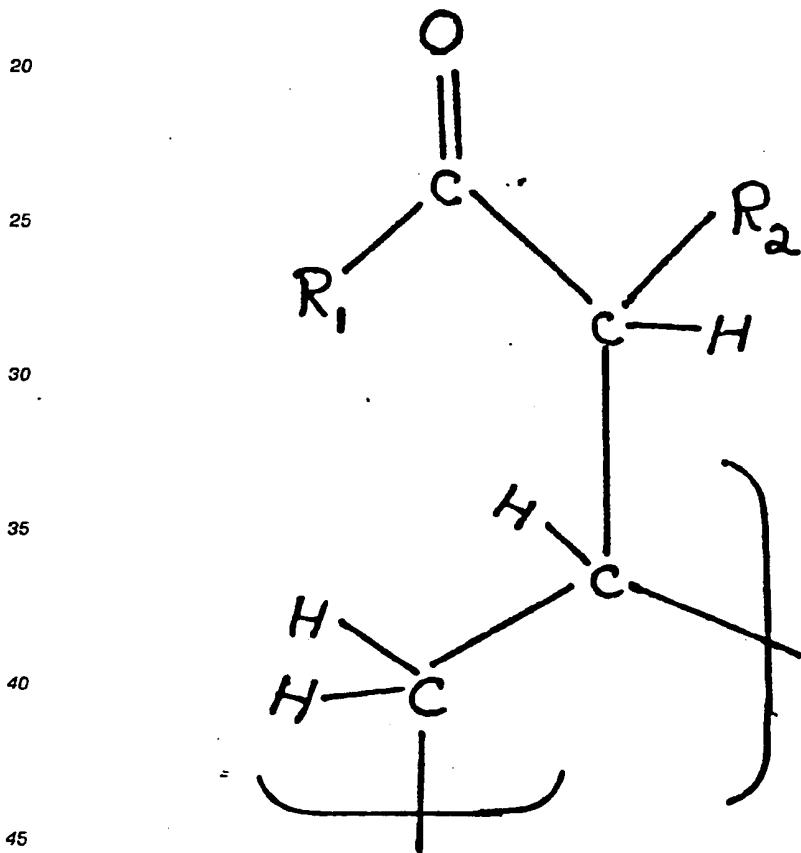
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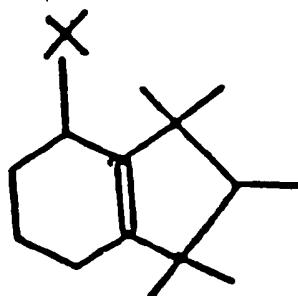


and



wherein R<sub>2</sub> is hydrogen; wherein R<sub>1</sub> is the moiety:  
 -OR<sub>3</sub> ;  
 50 wherein R<sub>3</sub> is selected from the group consisting of methyl and ethyl.  
 3. The compound of Claim 1 having the structure:

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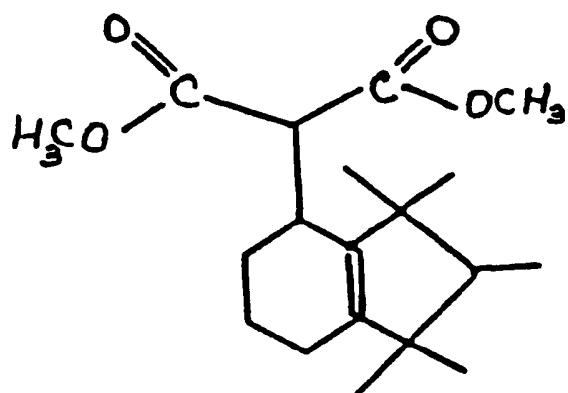
wherein X is chloro or bromo.

4. The compound of Claim 1 having the structure:

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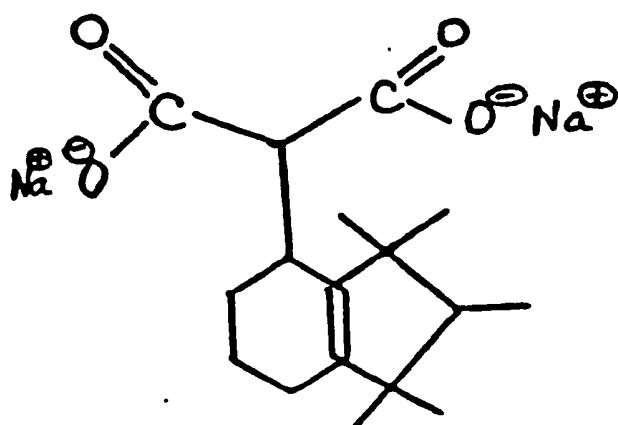
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5. The compound of Claim 1 having the structure:

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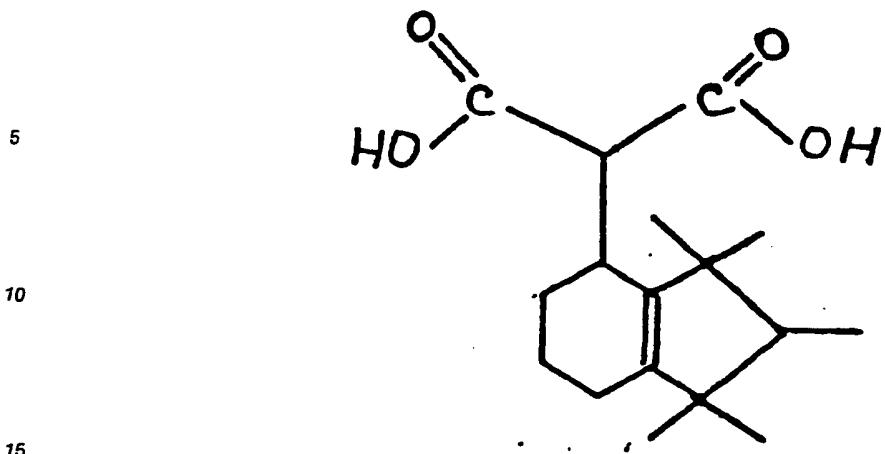
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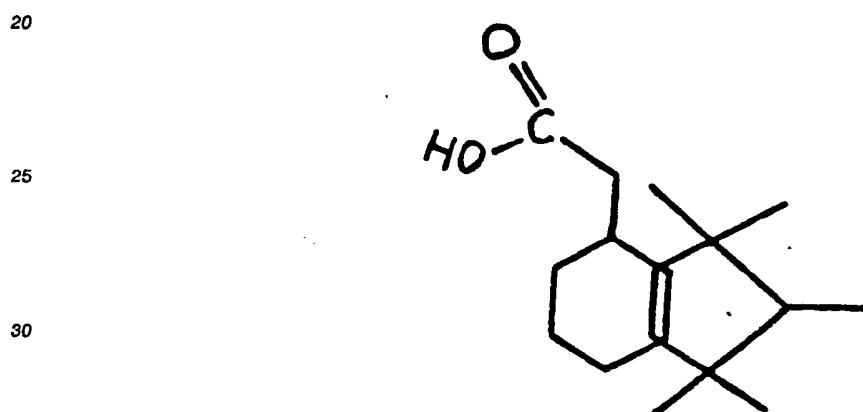
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6. The compound of Claim 1 having the structure:

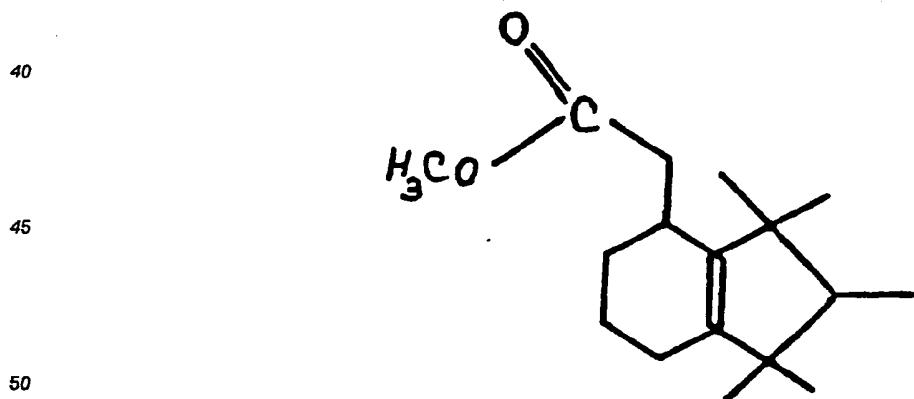
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7. The compound of Claim 1 having the structure:

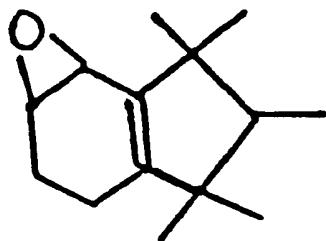


8. The compound of Claim 1 having the structure:



9. The compound of Claim 1 having the structure:

5



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10. A process for augmenting or enhancing the aroma of a perfume composition, cologne or perfumed article comprising the step of adding to a perfume base, a cologne base or a perfumed article base, an aroma augmenting or enhancing quantity of a compound defined according to Claim 2.

11. The compound of Claim 3 wherein X is chloro.

15 12. A process for reacting a compound of Claim 3 with at least one reagent capable of reacting with said compound whereby at least one composition having a utility in the perfumery art is produced.

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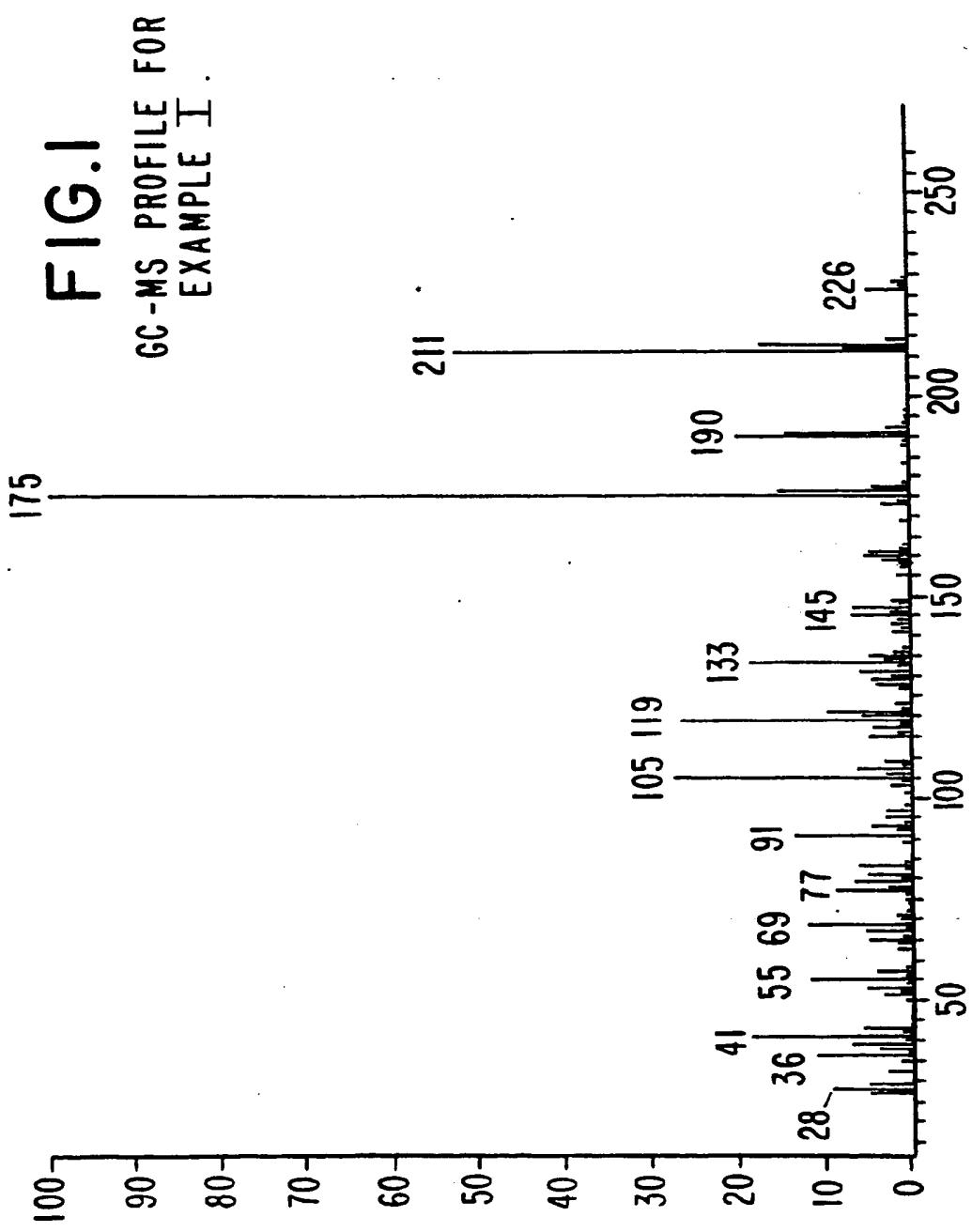
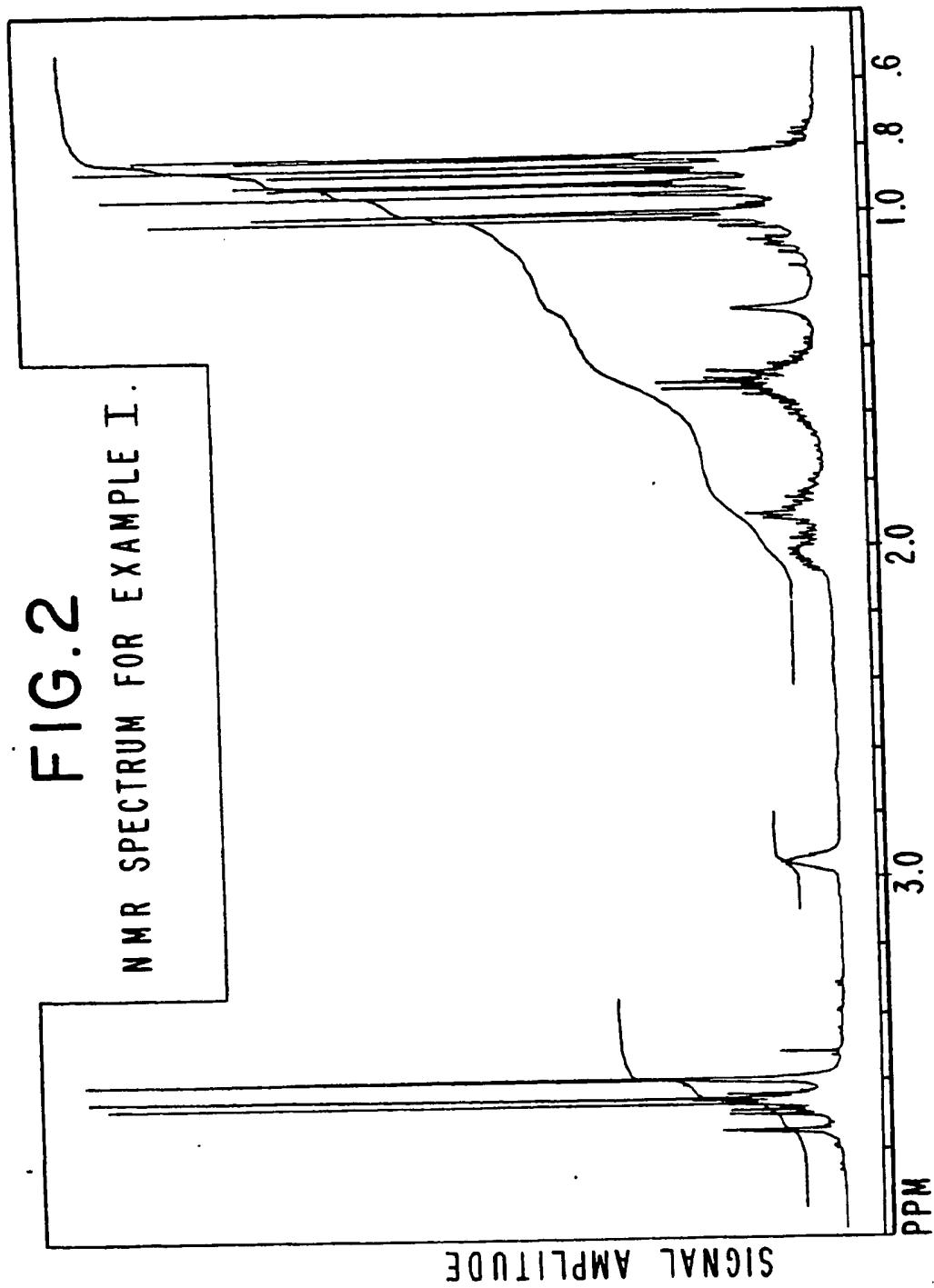


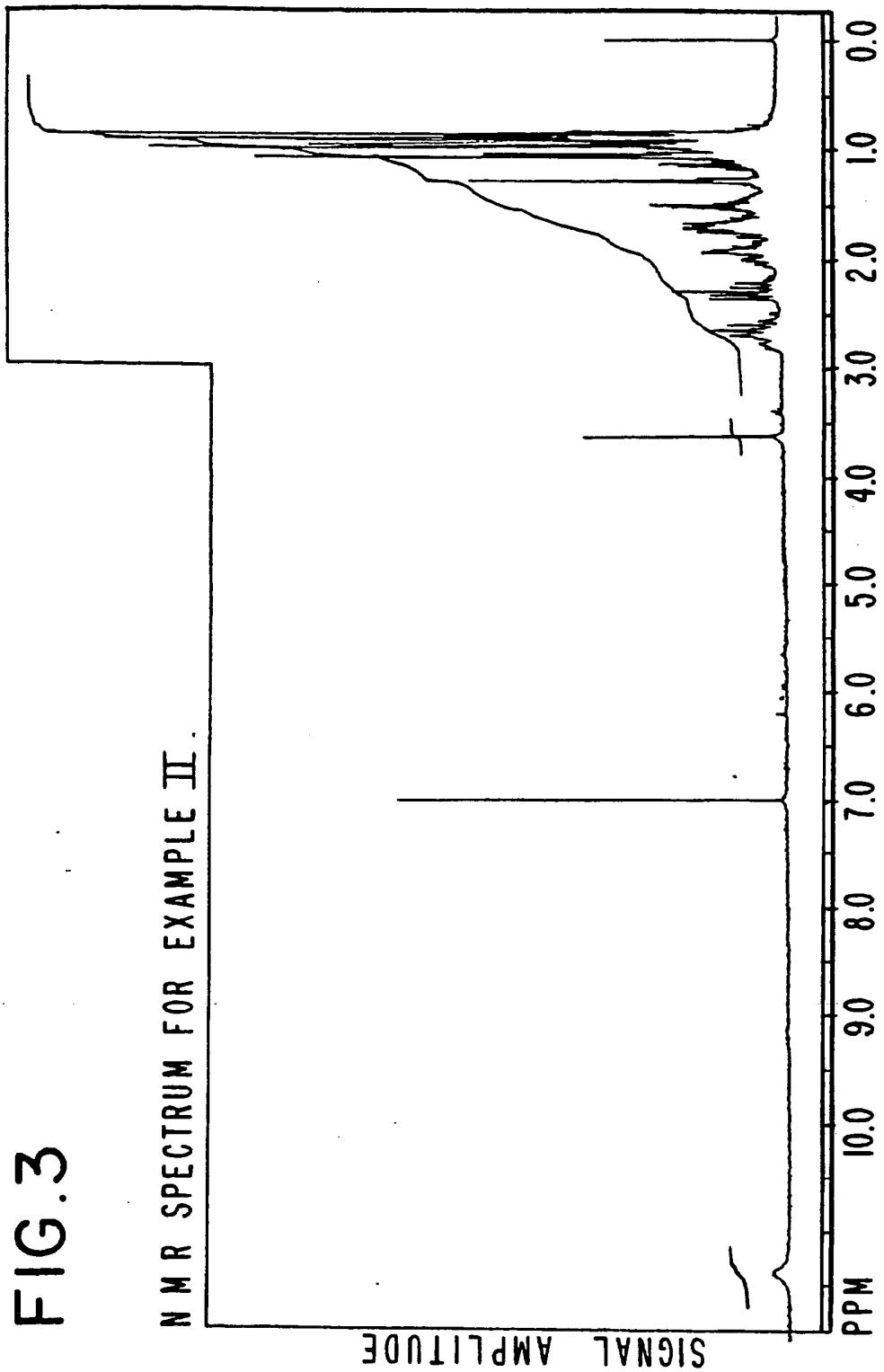
FIG. 2  
NMR SPECTRUM FOR EXAMPLE I.



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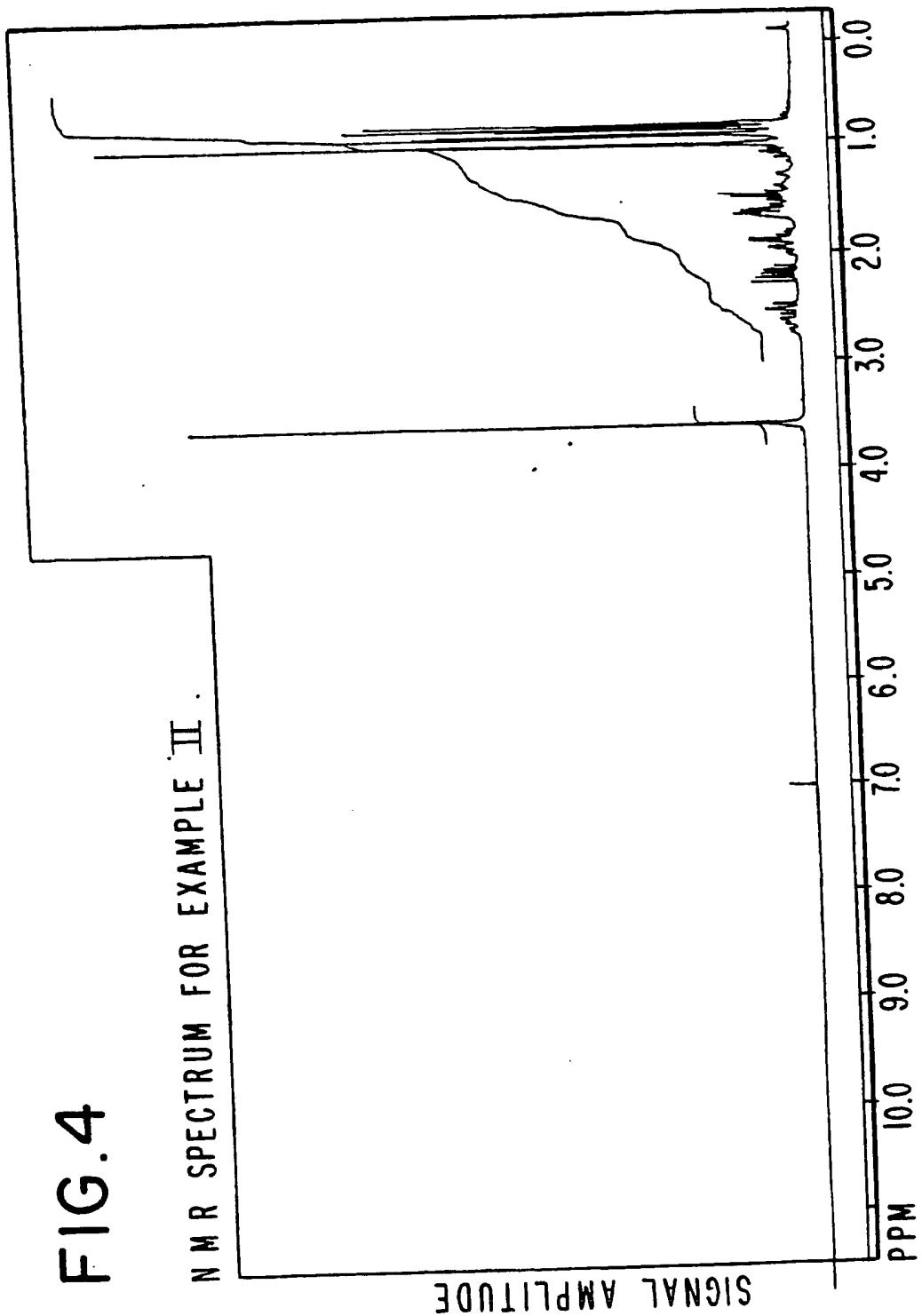
FIG. 3

N M R SPECTRUM FOR EXAMPLE III.



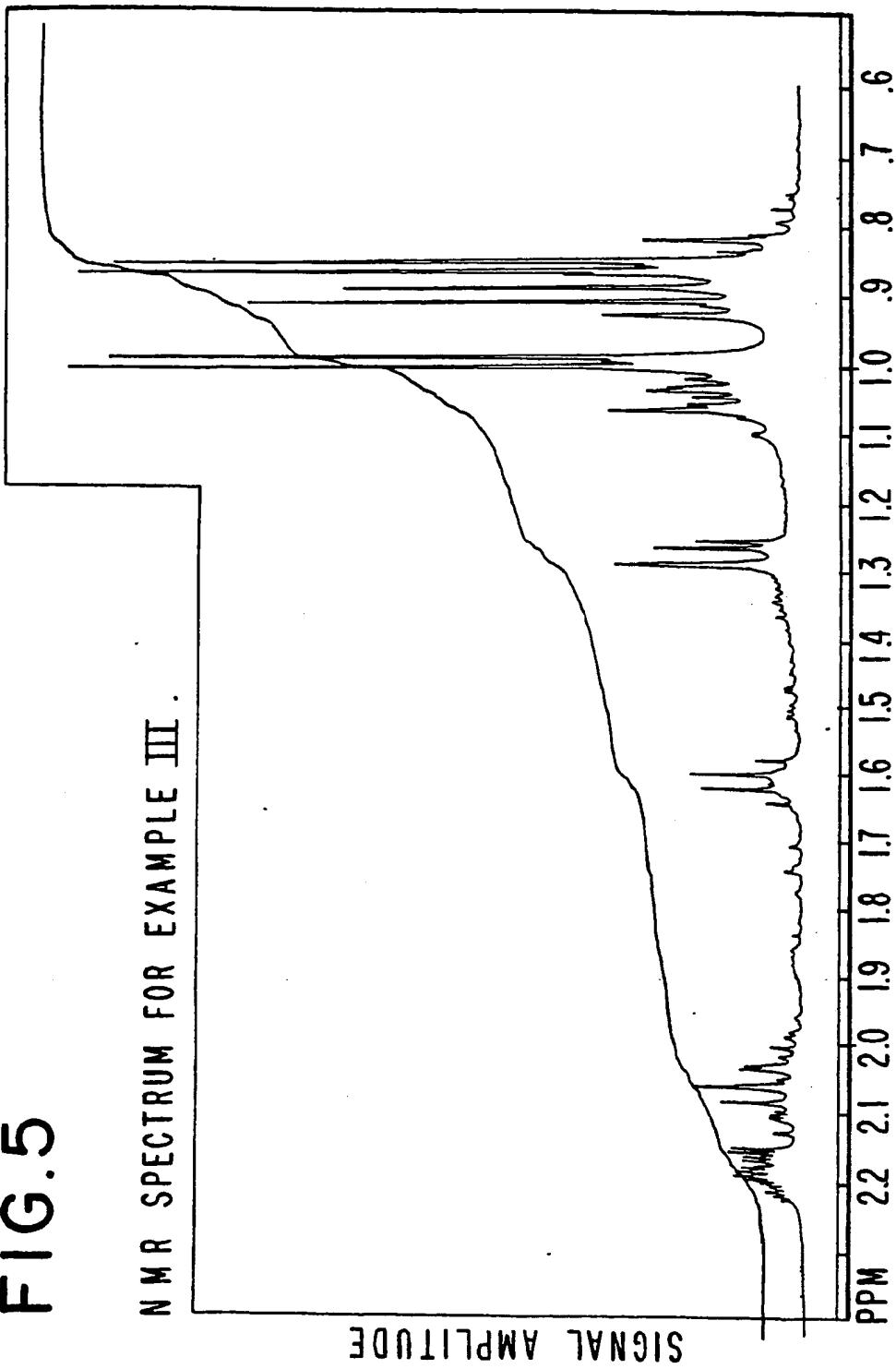
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FIG. 4  
N M R SPECTRUM FOR EXAMPLE II.



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FIG. 5



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FIG. 6

NMR SPECTRUM FOR EXAMPLE IV.

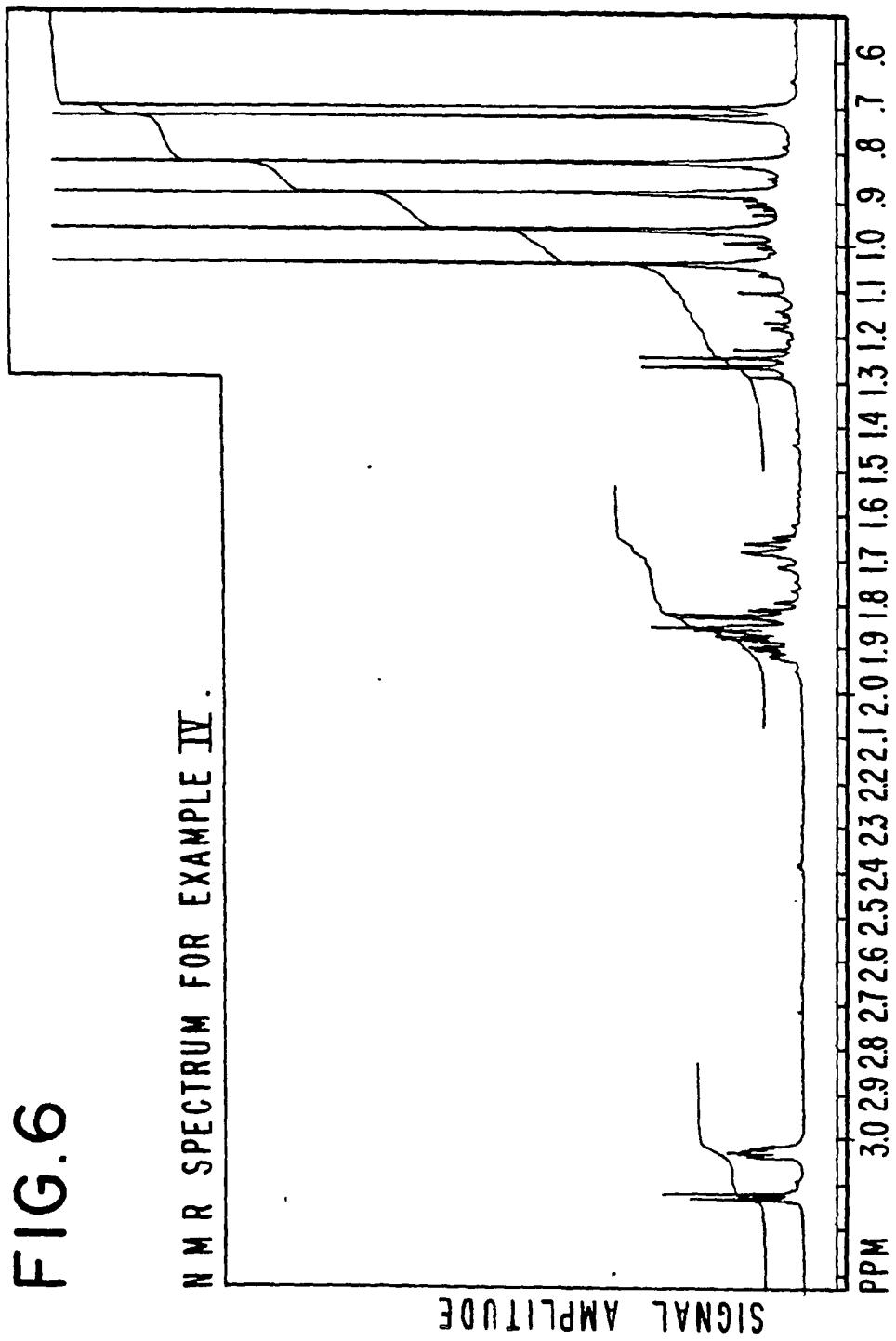


FIG. 7

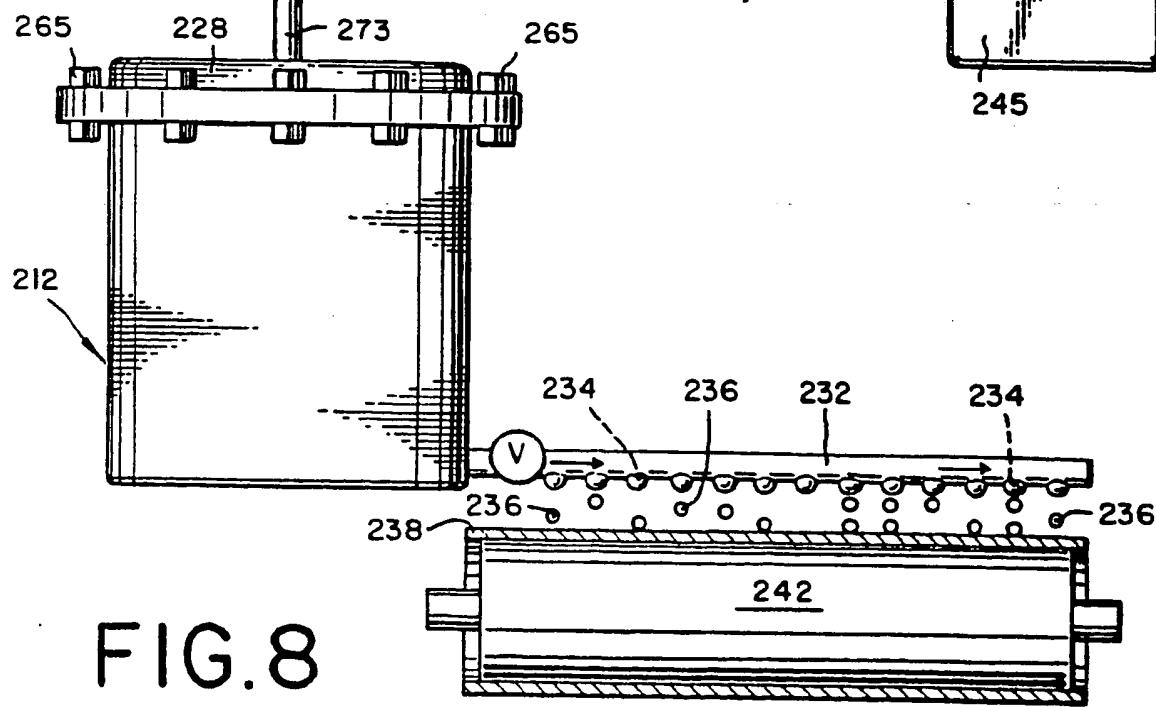
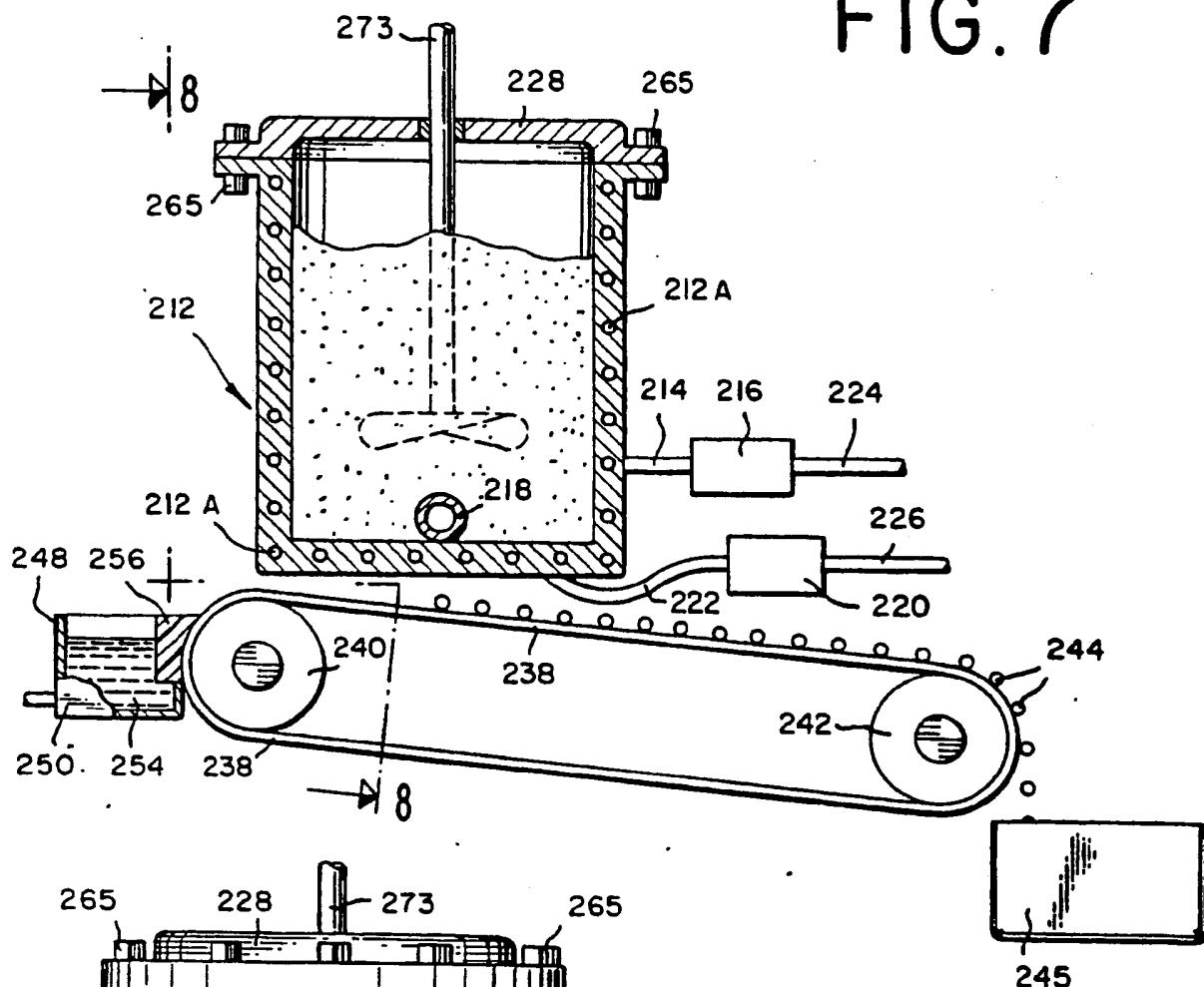


FIG. 8



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application number:

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 90301963.6
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl.)
A	<u>DE - A - 2 036 936</u> (INTERNATIONAL FLAVORS) * Examples 1-3,5,12,14 * --	1,10	C 07 C 23/34 C 07 C 69/608 C 07 D 303/04 C 07 C 57/26 C 11 B 9/00
A	<u>DE - A - 2 064 919</u> (INTERNATIONAL FLAVORS) * Examples 1-3,6 * --	1,10	
D,A	<u>US - A - 3 806 472</u> (J.B.HALL) * Claim * -----	1,10	
TECHNICAL FIELDS SEARCHED (Int Cl.)			
C 07 C 23/00 C 07 C 69/00 C 07 C 57/00 C 07 D 303/00			
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
VIENNA	16-05-1990	KÖRBER	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : technological background O : non-written disclosure P : intermediate document & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			



**Preparation of 1,1-disubstituted -1,2,3,4-tetrahydronaphthalene by addition action of toluene derivatives with 1,3-butadiene or its derivatives and cyclization.** Sato, Toshio; Takeda, Kyoichi. (Sumikin Kako K. K., Japan). Jpn. Kokai Tokkyo Koho (1997), 8 pp. CODEN: JKXXAF JP 09249584 A2 19970922 Heisei. Patent written in Japanese. Application: JP 96-62744 19960319. CAN 127:278071 AN 1997:632822 CAPLUS (Copyright 2001 ACS)

#### Patent Family Information

<u>Patent No.</u>	<u>Kind</u>	<u>Date</u>	<u>Application No.</u>	<u>Date</u>
JP 09249584	A2	19970922	JP 1996-62744	19960319

#### Abstract

The title compds. [I and II; R1, R2 = H, alkyl, alkoxy, alkoxyalkyl, (un)substituted aryl, aryloxy, aryloxyalkyl; one of R1 and R2 may form a ring which is linked to the carbon atom adjacent to the carbon atom linked to CHR1R2; Z = substituent or arom. fused ring stable under the reaction conditions; n = 0, 1-4; when n ≥ 2, each Z may be same or different to each other; R3, R4 = H, alkyl, alkoxy, alkoxyalkyl, (un)substituted aryl, aryloxy, aryloxyalkyl; when at least one of R1 and R2 = H, at least one of R3 and R4 ≠ H] are prepd. by addn. reaction of arom. compds. having a benzylic hydrogen (III; R1, R2, = same as above; m = 1-5; n = 0, 1-4; m+n ≤ 5; when m, n ≥ 2, each CHR1R2 or Z may be same or different to each other and at least one of the carbon atoms adjacent to the carbon atom linked to at least one CHR1R2 is not substituted) with butadiene CH2:CR4CR3:CH2 in the presence of an anionic basic addn. catalyst and cyclization of the resulting 1:1 adducts (IV and V; R1 - R4, Z, n = same as above) under heating in the presence of an acid catalyst. These compds. I and II are useful as intermediates for cosmetics, drugs, and agrochems. Thus, Na metal (catalyst) 1.07, K metal (catalyst) 3.73, biphenyl (catalyst aid) 4.4 g, and 200 mL THF were placed in a flask and heated to 60° under stirring, followed by adding 184 g toluene and then dropwise a soln. of 82 g 2-methyl-1,3-butadiene (isoprene) in 200 mL THF over 3 h, and the resulting mixt. was stirred at 60° for 1 h, cooled to 25° and treated with 100 mL H2O to decomp. the catalysts to give, after workup, 166.5 g adducts contg. two adducts as the main components. The latter adducts were autoclaved in the presence of 8.7 g silica alumina catalyst (N-633L, Nikki Chem., Japan) at 170° for 2 h to give 29.8% 1,1-dimethyl-1,2,3,4-tetrahydronaphthalene and 8.4% 1,2-dimethyl-1,2,3,4-tetrahydronaphthalene.

